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THERMAL REACTIONS OF HALOGENATED CARBOHYDRATES

By

Charles Richard Nelson

B.S., North Carolina State University, 1970

Presented in partial fulfillment of the requirements for the degree of

Master of Science

UNIVERSITY OF MONTANA

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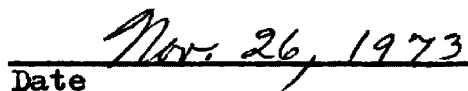
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CHAPTER I

INTRODUCTION

The theoretical and practical significance of the thermal reactions of carbohydrates relate to the problems of uncontrolled cellulosic fires, which present a major hazard to mankind and his environment. The initiation and propagation of these cellulosic fires take place through complex molecular transformations, resulting from the interaction of the fuel with energy and the environment.¹

Cellulosic materials, as such, are not flammable and do not burn directly.^{2,3} Initially, in the presence of a sufficiently powerful source of ignition, the polysaccharides present undergo thermal degradation resulting in the production of, among other products, combustible gases and vapors. These volatile pyrolysis products are then ignited in the gas phase with resultant diffusive burning known as flaming combustion.^{4,5} Competing reactions, which form water and char at the expense of the combustible volatiles, suppress the flaming combustion and rapid spread of fire.¹

The temperature at which the polysaccharides present in the cellulosic fuels begin to char is usually lower than the ignition temperature; thus, combustion is usually preceded by destructive distillation so that combustion of cellulosic materials is really the combustion of the products of its thermal decomposition.² The primary reactions of the polysaccharides during this thermal decomposition are different in oxidative

and inert atmospheres.⁷ The secondary reactions that give rise to the volatile products were found to be non-oxidative in nature, since the pyrolysis of cellulose in atmospheres of air, nitrogen, and helium gave essentially the same products.⁸ Since pyrolysis of various monosaccharides, disaccharides and polysaccharides have been found to yield the same mixture of volatile degradation products^{9,10,11,12,13}, a single crucial step in the decomposition appears to be similar for all these compounds.

Detailed thermal analysis combined with parallel chemical investigations have revealed to a large extent the sequence and nature of the complex concurrent and consecutive thermal reactions involved in the decomposition of carbohydrates.^{6,10,11,12,13,14,15,16,17,18,19} The thermal stability of glycosides and the kinetics of the pyrolysis process have been shown to be related to the electron density of the glycosidic bond.^{14,15} The decomposition reaction is initiated by the cleavage of the glycosidic linkage followed by a transglycosylation¹⁶ (or recoupling) process where the remaining free hydroxyl groups reform the glycosidic bonds at different locations. In this way the original molecule or macromolecule is broken down into a heterogeneous mixture of anhydro sugars and oligosaccharides that comprise the tar component of the combustible volatile products which can further break down to form char, water, carbon dioxide, and other low molecular weight volatile products.

The introduction of various substituent groups to, or the modification of, the basic glucose unit have been found to alter the nature of the thermal reactions involved in the decomposition of the carbohydrate compounds. Whereas O-glycosides break down to form volatile

combustible products, it has been found the N-glycosides²⁰ (glycosylamines) and other amino sugars¹⁶ (in comparison to the normal sugars) decompose at lower temperatures, undergo extensive dehydration reactions, produce substantial amounts of char and very little or no fragmentation products.

The introduction of an unsaturation or a carbonyl function in the sugar unit¹³ (3-deoxyhexosulose) resulted in the facile formation of water and char during pyrolysis. Similarly, phosphate-containing carbohydrate derivatives²¹, when pyrolyzed, exhibited a drastic reduction in the formation of combustible tars and increased amounts of char and water.

The presence of acidic and basic additives^{1,10,13,14,21,22,23} interfere in different ways with the normal thermal decomposition reactions, the overall results being that alternative pathways for the decomposition of the substrate are promoted instead of the normal transglycosylation process. Kinetically, the general effect of the additive is to lower the activation energy²⁴ of the overall thermal decomposition process. Consequently, the subsequent decomposition reactions proceed through a low energy pathway, involving dehydration and charring rather than the higher energy pathway involving fragmentation to combustible volatile products.^{11,18}

Recognition and understanding of the thermal reactions and the competing pathways involved in combustion of carbohydrates has significant implications in understanding the principal factors involved in the spreading of fire and methods of controlling it. The former aspect relates to fire dynamics while the latter aspect relates to the mechanism of flameproofing.

Theoretically, flameproofing may be achieved in two different ways.¹ One way is to prevent the pyrolysis of the solid substrate to form volatile flammable products, and the other is to retard combustion of the volatile products in the gas phase. At the substrate level, then, flameproofing could be achieved either by preventing the transglycosylation reaction or by initiating the dehydration reactions.

Amino groups^{16,20} interfere with the transglycosylation reaction by reacting with the glycosidic bonds or the potential carbonyl groups to give glycosylamines which rearrange with the formation of a double bond and subsequent dehydration and charring. Phosphate groups²¹, on the other hand, produce a catalytic effect by reacting with sugar molecules to form an ester and the resulting ester readily decomposes to form char and water and regenerate the phosphate group which will phosphorylate another sugar unit.

The mechanisms by which other well known and effective fire retardant compounds react, however, is not as well understood as those for the amino groups and phosphate compounds. Zinc chloride and other similar Lewis acids²⁵, for example, are known to be effective in retarding the combustion of cellulosic materials. Additionally, Lewis acids are effective in catalyzing the dehydration reactions and forming char and furan compounds (partially dehydrated sugars).^{1,3,6,10,11,18} Nevertheless, the important questions concerning whether the Lewis acid reacts with the substrate, interferes with the transglycosylation reaction, or reacts with the tar fraction of the volatiles remain unanswered. Additionally, halogens are effective free radical scavengers^{1,3} and could react with

the volatiles in the gas phase to retard combustion. In any event, the dehydration hypothesis¹ provides only a gross generalization of the flameproofing mechanism of Lewis acids.

In order to provide intelligent leads and a scientific basis for employing halogen-containing compounds and Lewis acids as a means of coping with fire problems, a systematic investigation of the thermal reactions of model carbohydrates modified to contain a halogen atom (a frequent component of Lewis acids) was conducted. Modified model compounds were used in order to investigate the effect of the halogen at the molecular level. Incorporation of the halogen atom as a part of the substrate in this way will permit evaluation of the role of the combined halogen in promoting charring and dehydration of the substrate and, if the halogen is eliminated from the substrate, how the halogen enters into the gas phase of the pyrolytic reaction.

The study involved an investigation of the thermal reactions of 6-chloro-6-deoxy-D-glucopyranose and related glycosides. Extensive thermal analysis was combined with parallel chemical investigations in order to determine the sequence and nature of the complex concurrent and consecutive thermal reactions involved in the decomposition of the substrate. Thus, two major approaches were involved: thermal analysis of the substrate and chemical analysis of the pyrolytic products.

In general, thermal analysis methods were useful for detecting the sequence of physical and chemical transformations which take place on heating the carbohydrate derivatives. Each of these events was then investigated by other methods to indicate the nature of the transformation taking place.

CHAPTER II

RESULTS

Thermal Analysis and Chemical Analysis After Heating of 6-chloro-6-deoxy- α -D- glucopyranose

The thermal analysis of crystalline 6-chloro-6-deoxy- α -D-glucopyranose is shown in Figure 1. The differential thermal analysis (dta), thermogravimetric analysis (tga), and derivative thermogravimetry (dtg) reflect the sequence of physical transformations and chemical reactions as the sugar is heated at the constant rate of 10°C/min. In this thermogram the dta curve contains an endotherm at 133°C, corresponding to the melting point of the compound. Unlike the thermogram of β -D-glucopyranose shown in Figure 2, however, a second endotherm follows directly after the melting at 141°C. The tga and dtg curves in Figure 1 show that the weight loss starts at about 135°C and reaches a maximum rate of 0.12 mg/min at 142°C. Following the rapid weight loss, there is a slow volatilization which leaves a fairly stable carbonaceous residue at 400°C amounting to 35% of the original material. This compares to a maximum rate of weight loss of 0.16 mg/min at 320°C and a 27% residue obtained from the β -D-glucopyranose.

The physical transformations and chemical reactions occurring during the melting and decomposition endotherms were further investigated by chemical analysis of the products of 6-chloro-6-deoxy- α -D-glucopyranose heated to several different temperatures before, during,

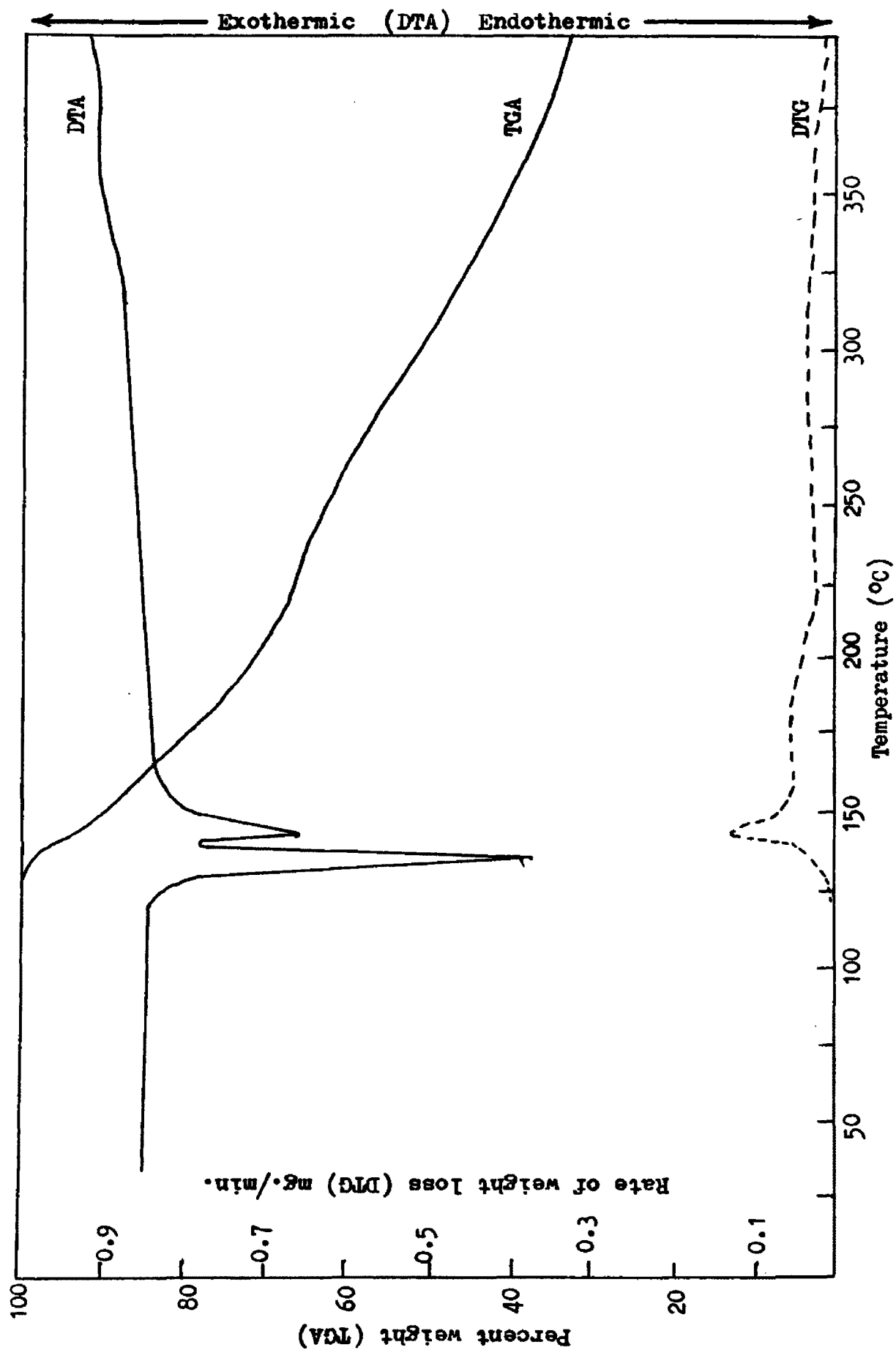


Figure 1.—Thermogram of 6-chloro-6-deoxy- α -D-glucopyranose.

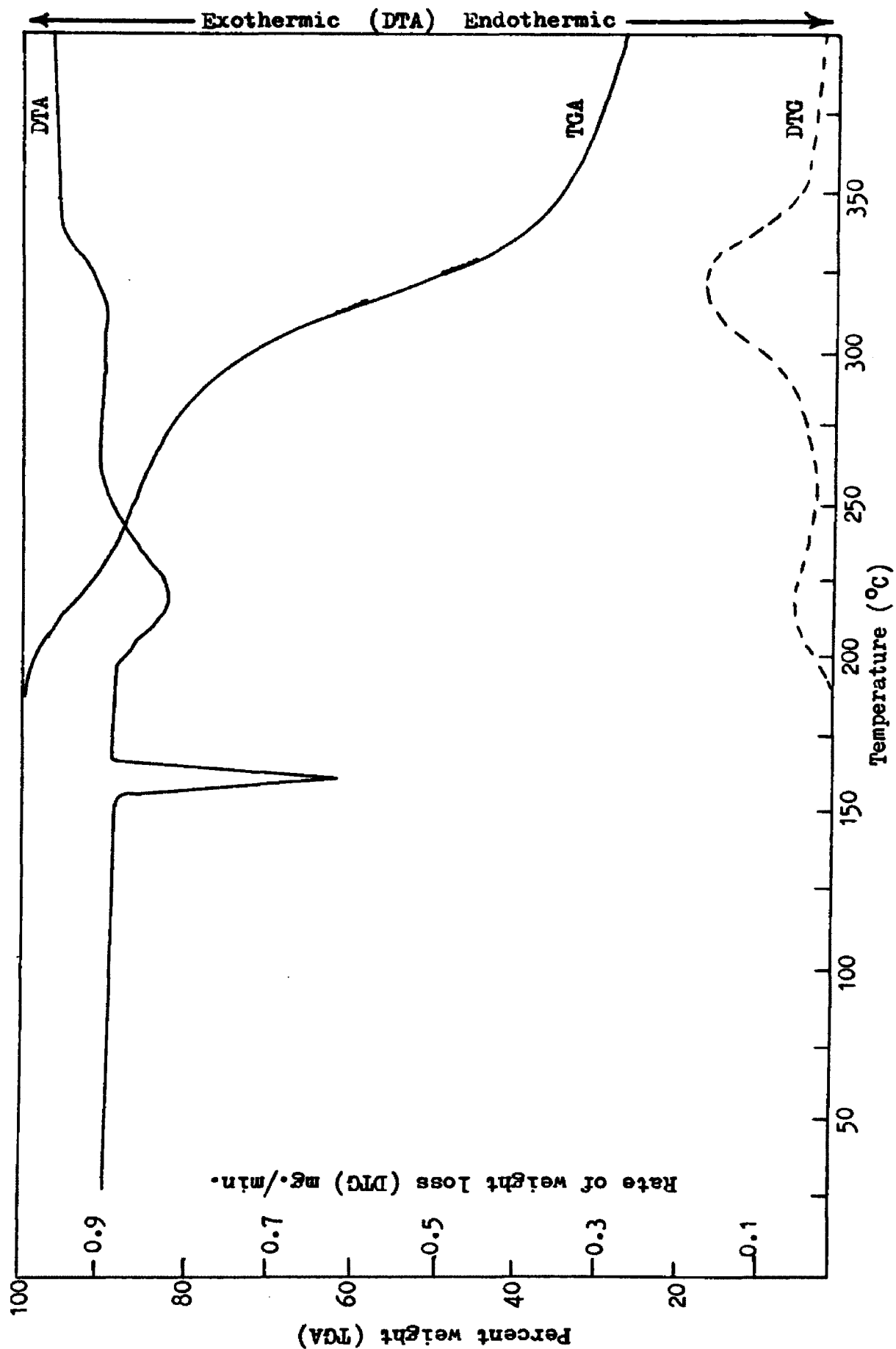


Figure 2.—Thermogram of β -D-glucopyranose.

and after the melting point and the decomposition. Thus, a series of products corresponding to different stages in the development of the endotherm were obtained that more accurately reflected the type of physical transformations or chemical reactions that were occurring. Trimethylsilylation and gas-liquid chromatography (glc) analysis of the heated samples gave the data shown in Table I.

TABLE I
ANALYSIS OF THE ANOMERS FORMED AT VARIOUS TEMPERATURES
FROM 6-CHLORO-6-DEOXY-D-GLUCOPYRANOSE

Temp (°C)	6-chloro-6-deoxy- α -D-glucopyranose		6-chloro-6-deoxy- β -D-glucopyranose	
	(ratio) ^a	(%) ^b	(ratio) ^c	(%) ^b
25.0	99.2	99.5	0.8	0.8
123.5	97.4	95.7	2.6	2.6
133.0	82.1	80.5	17.9	17.5
137.5	55.6	28.5	44.5	22.8
142.0	59.1	12.8	40.9	8.8
151.5	0.0	0.0	0.0	0.0

^aRatio of $\frac{\alpha}{\alpha+\beta}$ forms X 100.

^bBased on original material.

^cRatio of $\frac{\beta}{\alpha+\beta}$ forms X 100.

The combination of the data in Table I and Figure 1 show that the 6-chloro-6-deoxy- α -D-glucopyranose compound disappears much faster than could be accounted for by the weight loss (due to volatilization). This suggests that other non-volatile, higher molecular weight compounds must be produced both during melting and during decomposition. Samples of the carbohydrate compound were heated to the same temperatures as in Table I, dissolved in a minimum amount of absolute methanol and analyzed

by thin layer chromatography (tlc). The heated samples began to develop a continuous strip between the origin and the location of the 6-chloro-6-deoxy- α -D-glucopyranose. By the time the temperature reached 142.0°C the strip was a continuous line from the origin to a location beyond the point of the starting material. These pyrolysis products were hydrolyzable with acid to give a single TLC spot corresponding to 6-chloro-6-deoxy-D-glucopyranose, and for those samples heated above 133.0°C, additional faster moving spots.

Thermal Analysis and Chemical Analysis
After Heating of Methyl 6-chloro-6-
deoxy- α - and β -D-glucopyranoside

The thermograms of the crystalline methyl 6-chloro-6-deoxy-D-glucopyranoside anomers are shown in Figures 3 and 4, and those of the corresponding unsubstituted compounds are shown in Figures 5 and 6. The thermal analysis features of these compounds are shown in Table II.

The combination of data in Table II and Figures 3 and 4 indicate a pronounced difference in thermal behavior for the different anomers of methyl 6-chloro-6-deoxy-D-glucopyranoside. The β -anomer begins to decompose at very low temperatures and over a broad temperature range, while the α -anomer decomposes sharply at a much higher temperature. This is true also for the unsubstituted anomers but to a much smaller extent.

The maximum rates of decomposition shown by the dtg peaks from Table II and Figures 3 and 4 indicate that an apparent difference exists in the decomposition reactions of the α - and β -anomers of methyl 6-chloro-6-deoxy-D-glucopyranoside. Isothermal heating followed by chemical analysis was employed to further investigate this apparent difference in

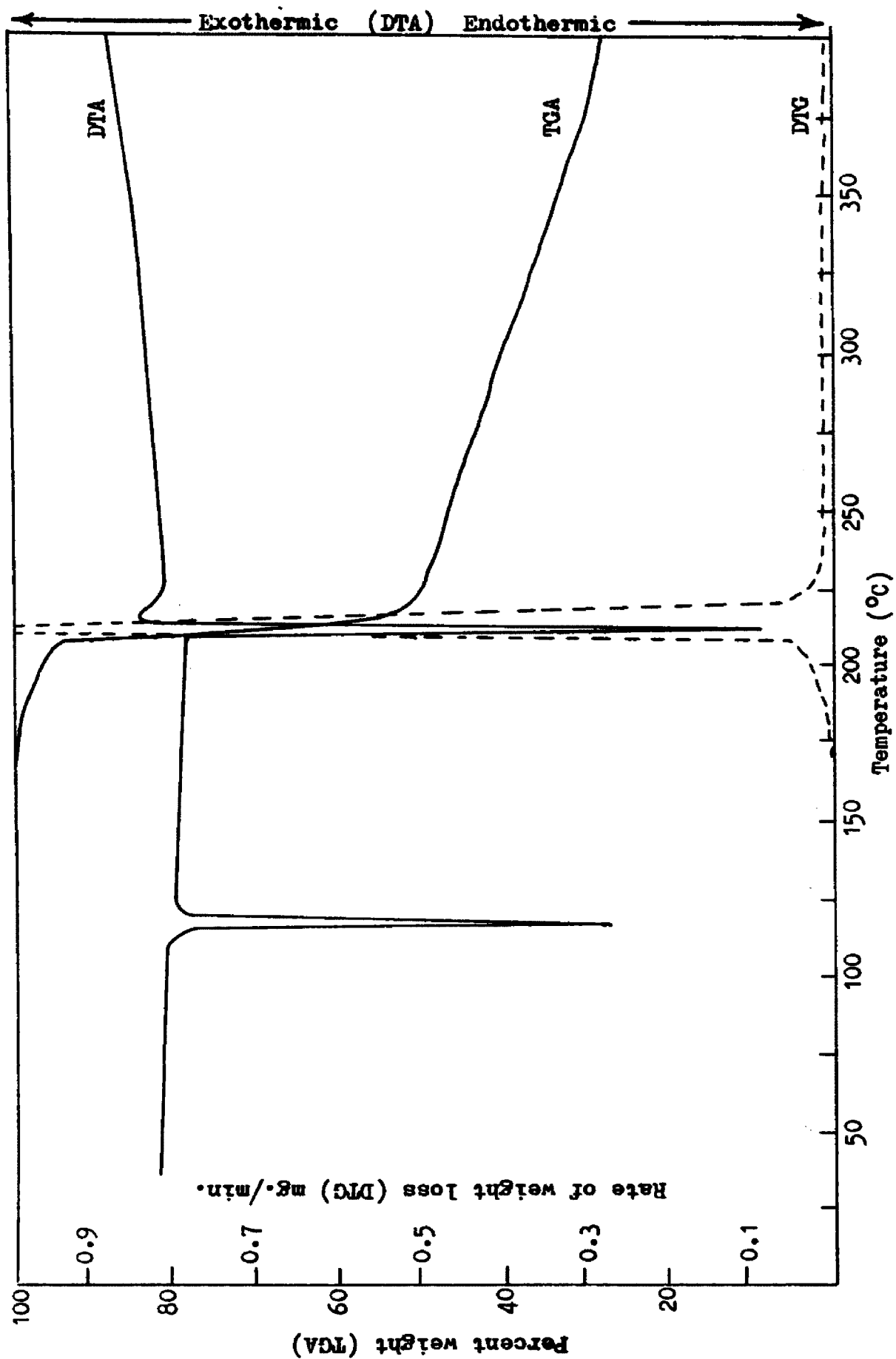


Figure 3.---Thermogram of methyl 6-chloro-6-deoxy- α -D-glucopyranoside.

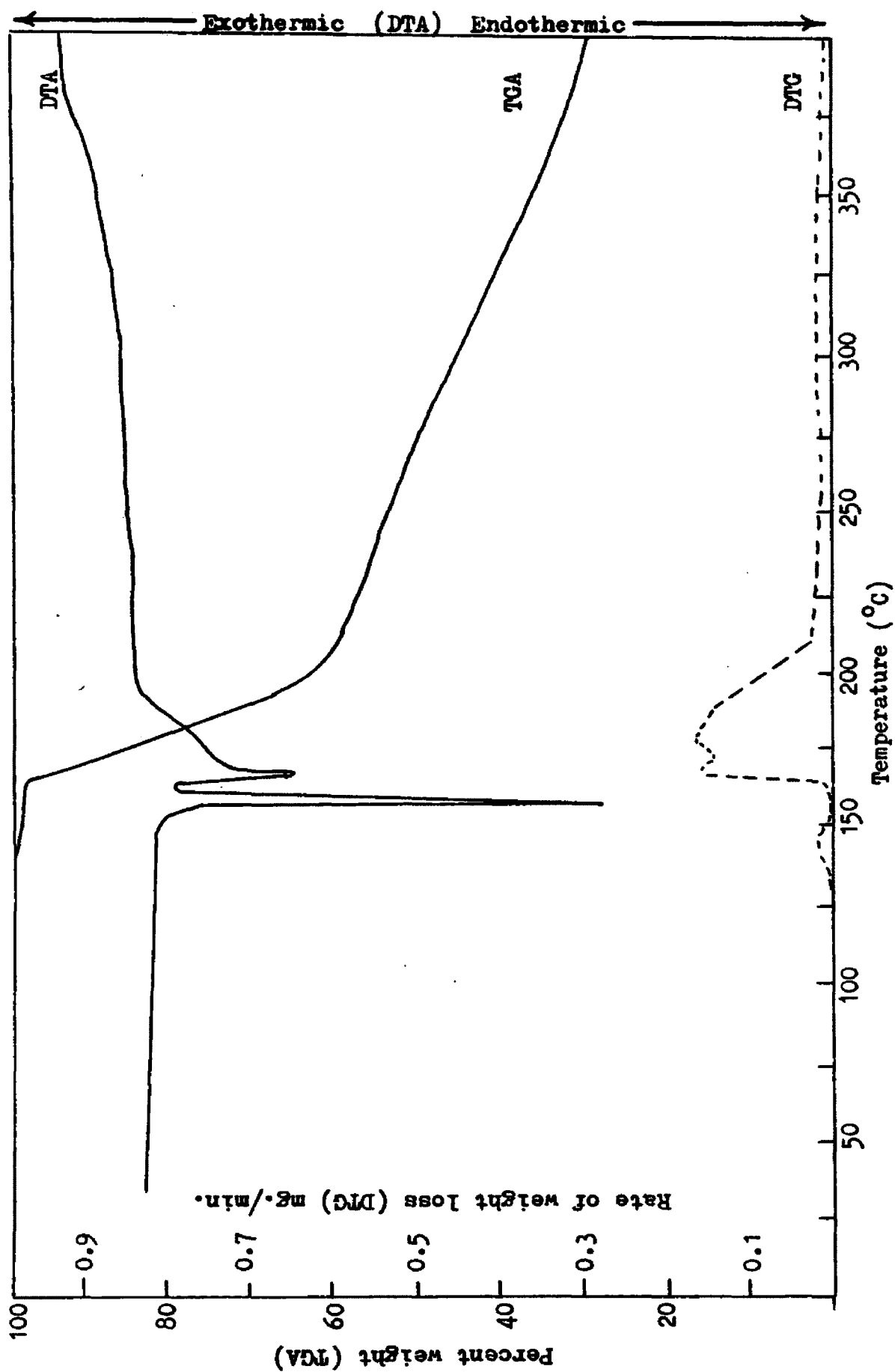


Figure 4.—Thermogram of methyl 6-chloro-6-deoxy-β-D-glucopyranoside.

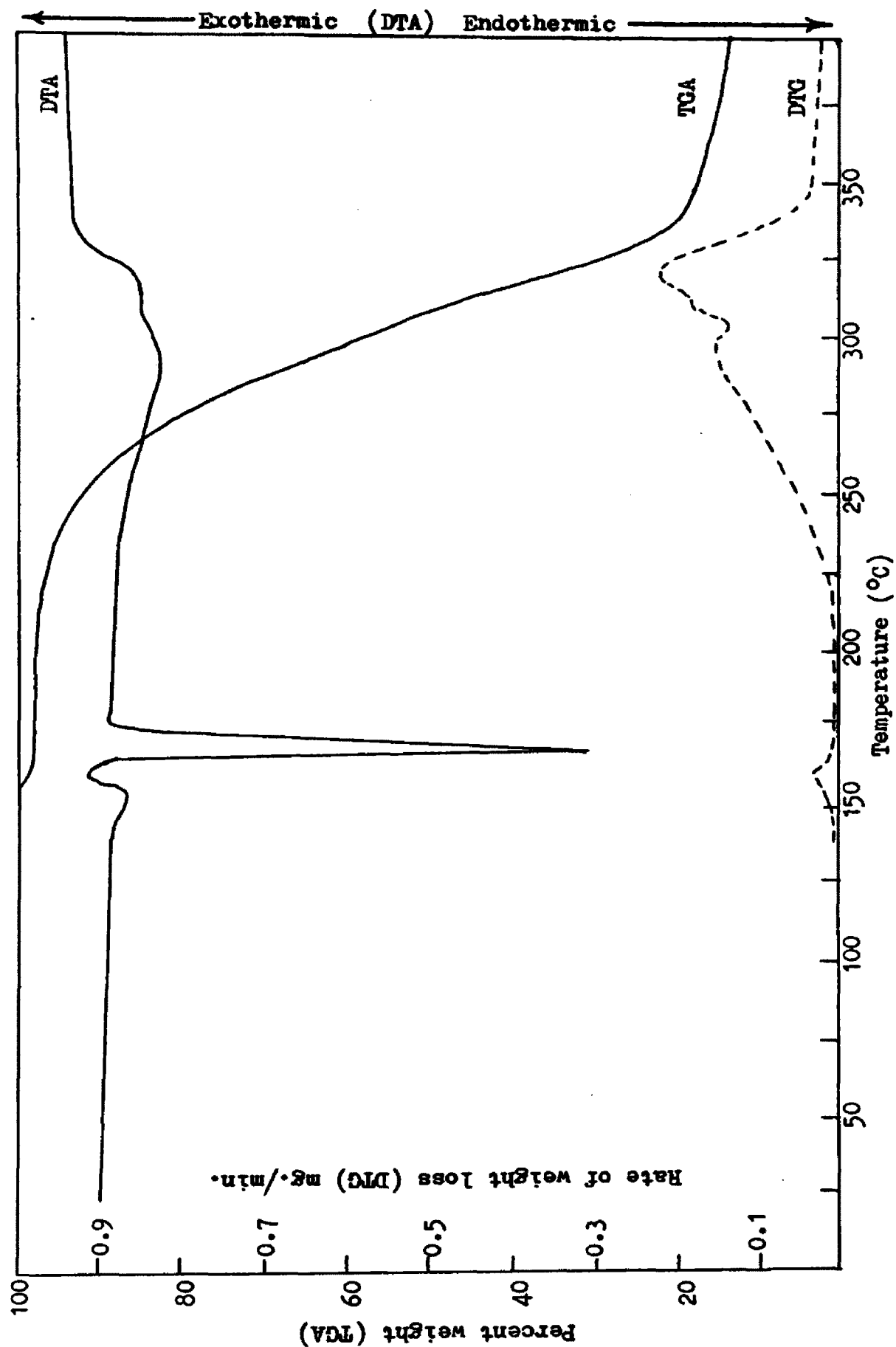


Figure 5.—Thermogram of methyl α -D-glucopyranoside.

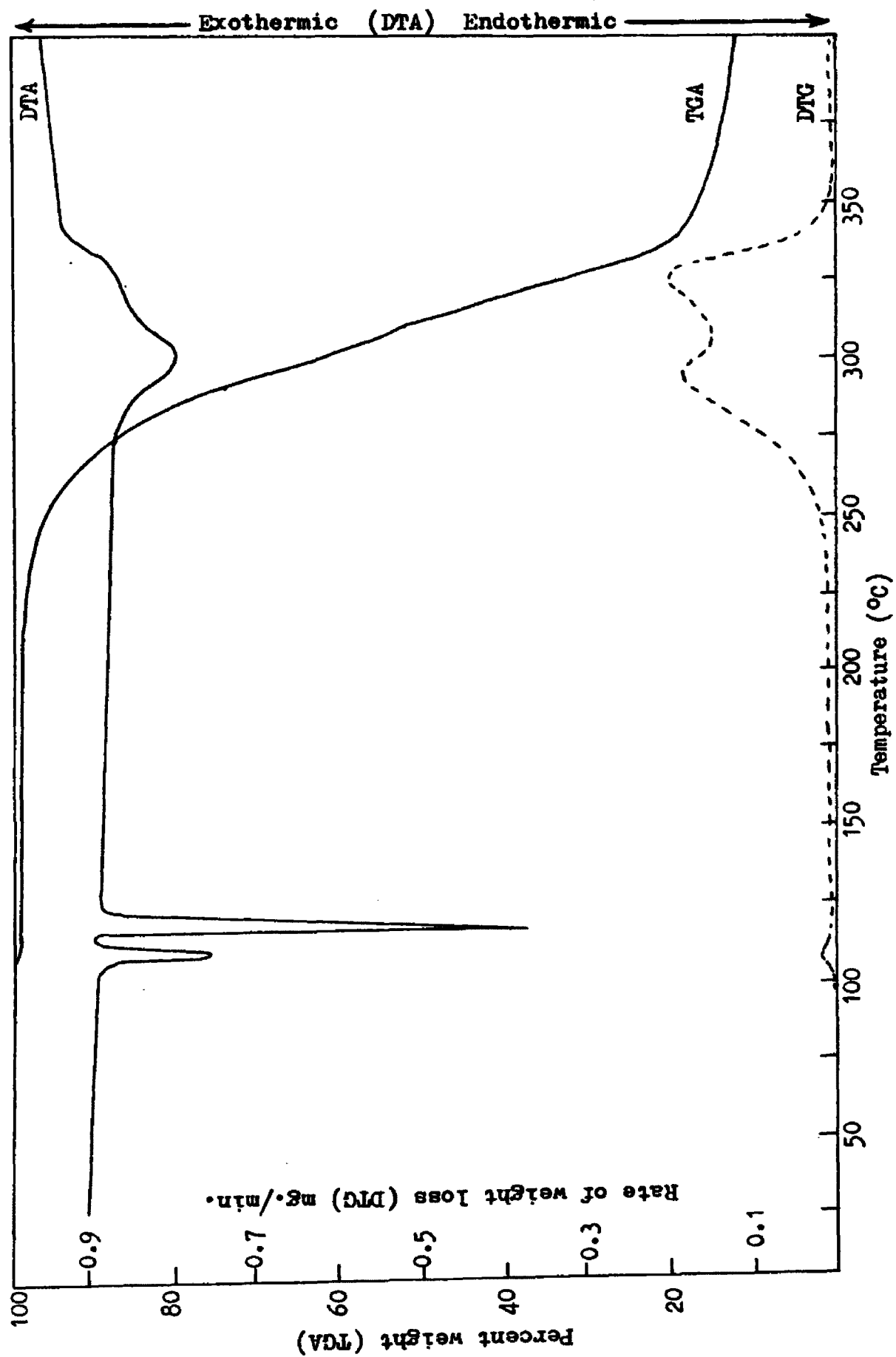


Figure 6.—Thermogram of methyl β-D-glucopyranoside.

TABLE II
THERMAL ANALYSIS FEATURES OF NORMAL AND
CHLORINATED METHYL GLYCOSIDES

Methyl Glycosides	Temperature of Dta Events					Dtg Dec, Rate of °C Wt loss, mg/min	Tga Residue ^a
	Transition, °C	Mp, °C	Threshold Dec, °C	1st Dec Point, °C	2nd Dec Point, °C		
6-chloro-6-deoxy- α - <u>D</u> -glucopyranoside		114	207	209	215 ^b	209 1.04	29
6-chloro-6-deoxy- β - <u>D</u> -glucopyranoside		156	160	164	170	177 0.20	32
α - <u>D</u> -glucopyranoside	155	167	220	290	315	295 0.16	17
β - <u>D</u> -glucopyranoside	106	115	230	298	325	295 0.20	14

^aPercent residue at 400°C based on anhydrous weight of the original material.

^bExothermic.

thermal decomposition reactions. Samples of both anomers were separately heated isothermally at various temperatures near the threshold decomposition point of the methyl 6-chloro-6-deoxy- β -D-glucopyranoside compound. Trimethylsilylation and glc analysis of the heated samples of methyl 6-chloro-6-deoxy- β -D-glucopyranoside gave the data shown in Table III.

The corresponding results for methyl 6-chloro-6-deoxy- α -D-glucopyranoside indicated a linear rate of weight loss with no decomposition. This corresponded to evaporation of the molecule at 156°C and 160°C and indicated that the α -anomer is thermally stable at these temperatures.

The data from Table III indicates that as methyl 6-chloro-6-deoxy- β -D-glucopyranoside decomposes, significant amounts of the α -anomer are formed. Graphs of this data from Table III are shown in Figures 7 and 8. The graphic presentations of the results indicate that following the initial decomposition of the substrate there is an induction period preceding the initial formation of the α -anomer. This induction period decreases as the temperature is increased. Logarithmic plots of the data from Table III, shown in Figures 9 and 10, indicate that the disappearance of the β -anomer does not follow simple first-order kinetics since the slope of the line changes abruptly shortly after the start of decomposition. This change in slope corresponds to the point at which the α -anomer first begins to appear.

The thermal reactions of methyl 6-chloro-6-deoxy- β -D-glucopyranoside were further investigated by isothermal heating at 160°C followed by uv analysis of methanolic solutions of the remaining residue. The results are shown in Figure 11. Methyl 6-chloro-6-deoxy- β -D-glucopyranoside

TABLE III
COMPOSITION OF THE THERMOLYSIS PRODUCTS FROM
METHYL 6-CHLORO-6-DEOXY- β -D-GLUCOPYRANOSIDE

Time (minutes)	Temp (°C)	β -Anomer (%)	α -Anomer (%)
0.0	156	100.0	0.0
0.5		95.8	0.0
1.0		78.3	0.0
1.5		57.0	trace
2.0		32.8	5.0
2.5		18.0	6.5
3.0		11.4	4.7
3.5		5.3	4.0
4.0		3.2	3.5
4.5		4.0	3.0
5.0		trace	1.0
0.0	160	100.0	0.0
0.5		97.7	0.0
1.0		64.6	trace
1.5		33.3	5.0
2.0		16.6	8.1
2.5		7.0	8.3
3.0		6.6	5.0
3.5		0.8	3.0
4.0		trace	2.0

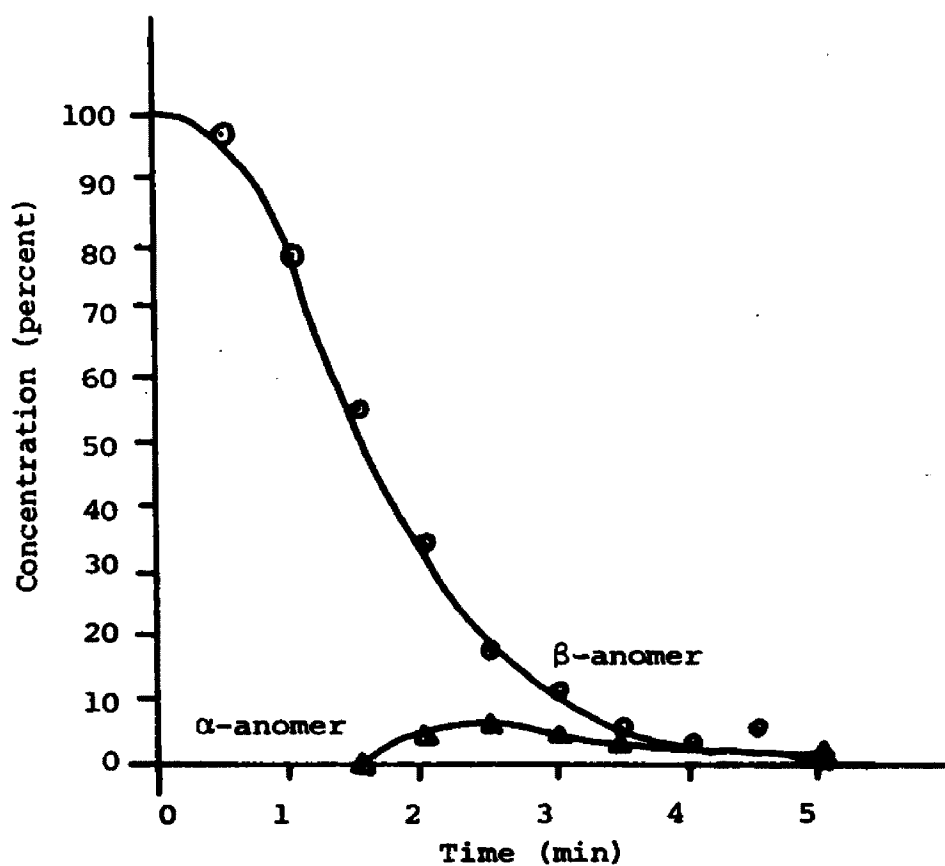


Figure 7.--Plot of concentration (%) vs. time at 156°C of the anomeric forms of methyl 6-chloro-6-deoxy-D-glucopyranoside.

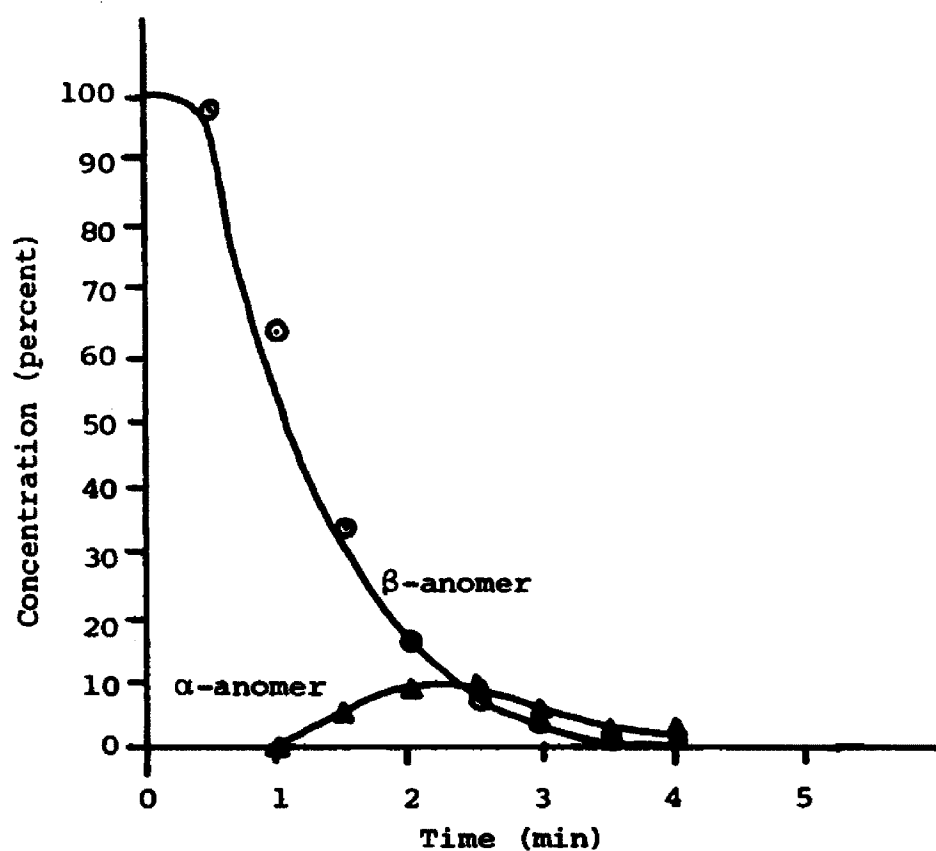


Figure 8.--Plot of concentration (%) vs. time at 160°C of the anomeric forms of methyl 6-chloro-6-deoxy-D-glucopyranoside.

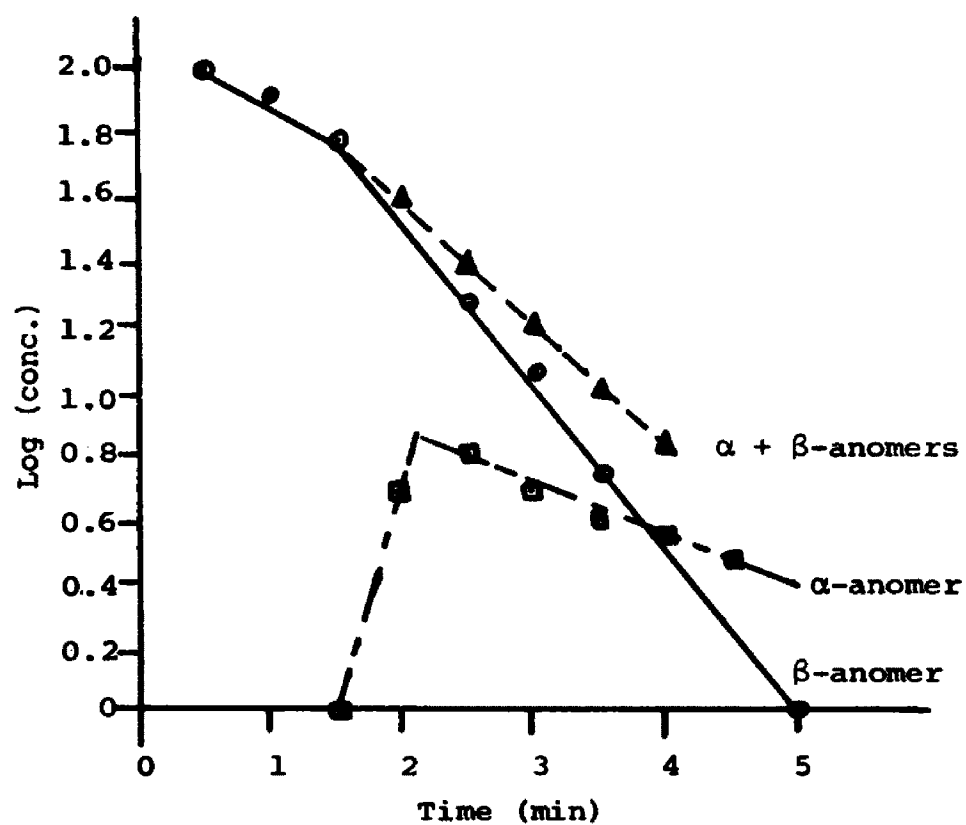


Figure 9.--Plot of Log (conc.) vs. time at 156°C of the anomeric forms of methyl 6-chloro-6-deoxy-D-glucopyranoside.

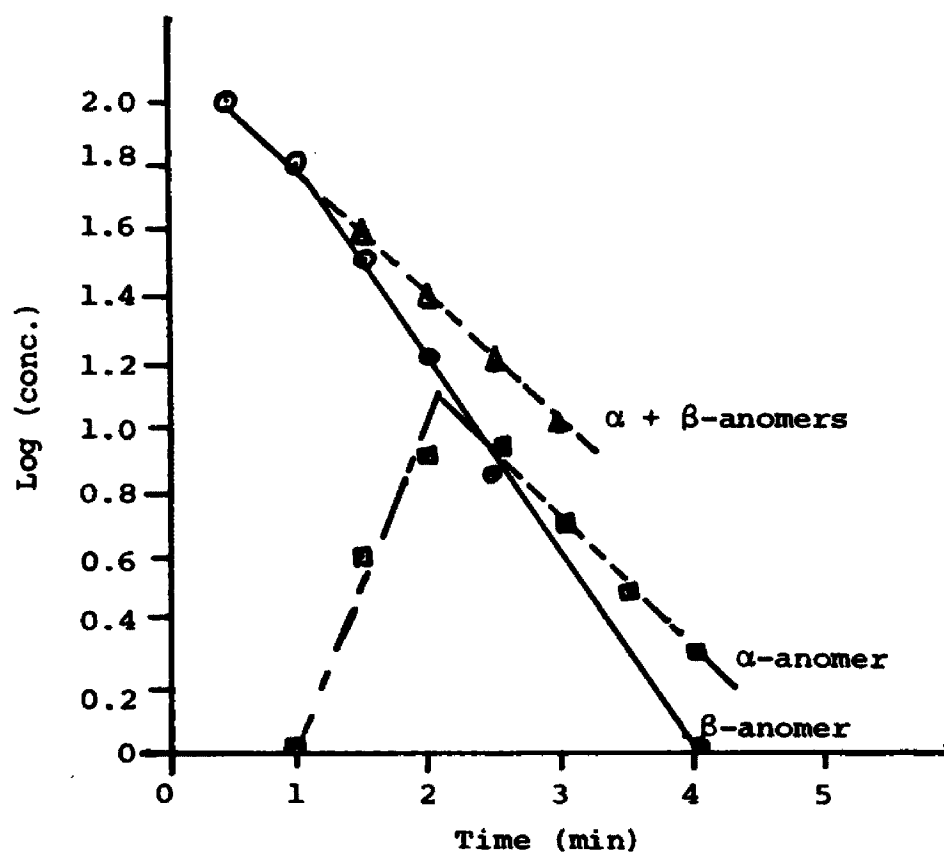


Figure 10.--Plot of Log (conc.) vs. time at 160°C of the anomeric forms of methyl 6-chloro-6-deoxy-D-glucopyranoside.

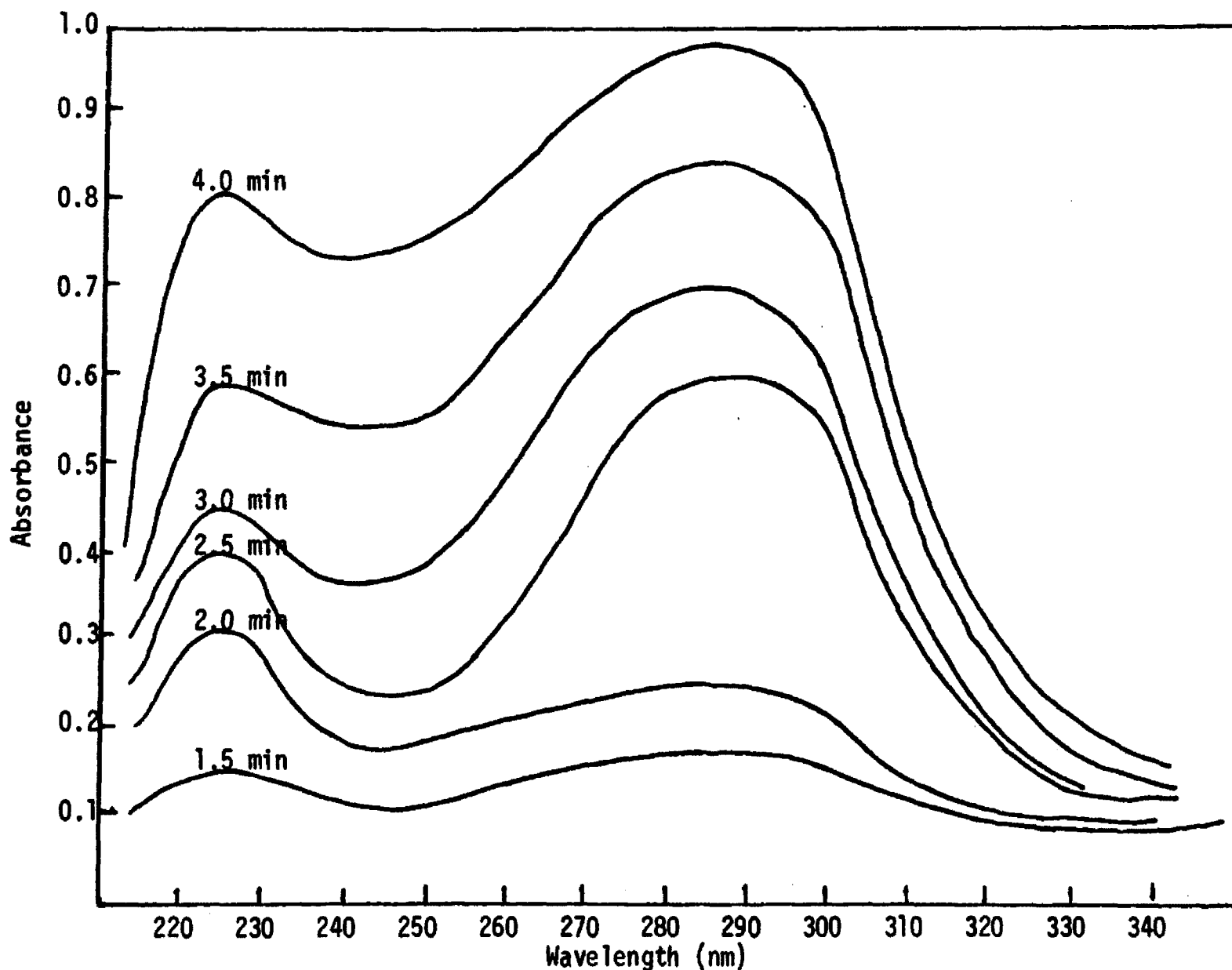


Figure 11.--Ultraviolet spectrum of isothermal pyrolysis of methyl 6-chloro-6-deoxy- β -D-glucopyranoside. The unheated material and the residues remaining after heating through the first minute exhibited no uv absorption.

exhibited no uv absorption, and the residues remaining after isothermal heating through the first minute also exhibited no uv absorption; however, further heating indicated that a chromophoric group absorbing in the region of 228 nm forms first, followed by formation of a second chromophoric group absorbing in the region of 290 nm.

Thermal Analysis and Chemical Analysis
After Heating of Phenyl 6-chloro-6-
deoxy- β -D-glucopyranoside

The thermograms of crystalline phenyl 6-chloro-6-deoxy- β -D-glucopyranoside and phenyl β -D-glucopyranoside are shown in Figures 12 and 13 respectively. The dta curve for phenyl 6-chloro-6-deoxy- β -D-glucopyranoside exhibits a sharp decomposition endotherm centered at 177°C; whereas, that for phenyl β -D-glucopyranoside is much broader and is centered at 290°C. The tga and dtg curves show that the weight loss for the former compound reached a maximum rate of 0.84 mg/min at 177°C compared to a maximum of 0.29 mg/min at 290°C for the latter compound. Following the rapid weight loss, there was a slow volatilization of the phenyl 6-chloro-6-deoxy- β -D-glucopyranoside resulting in 34% carbonaceous residue at 400°C. This compares to 17% residue obtained from the phenyl β -D-glucopyranoside.

Chemical analyses of the decomposition products were used to determine if cleavage of the glycosidic linkage occurred during decomposition. Using conditions identical with the dynamic dta and tga, the nitrogen purge gas was bubbled through 1.0 N NaOH solution in order to trap any liberated phenol. The resulting solutions were analyzed by uv absorption. The resulting data indicated that for

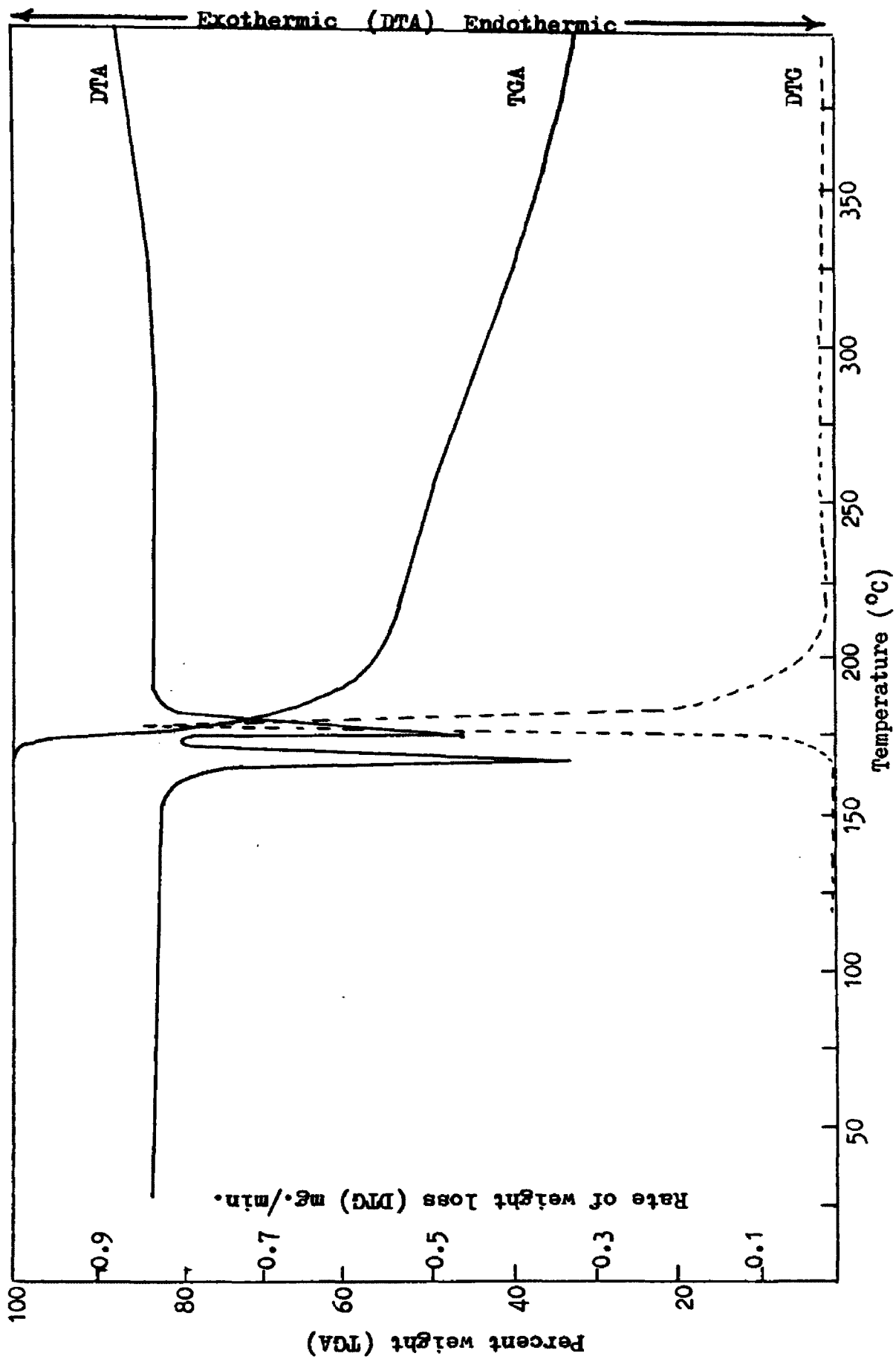


Figure 12.—Thermogram of phenyl 6-chloro-6-deoxy-β-D-glucopyranoside.

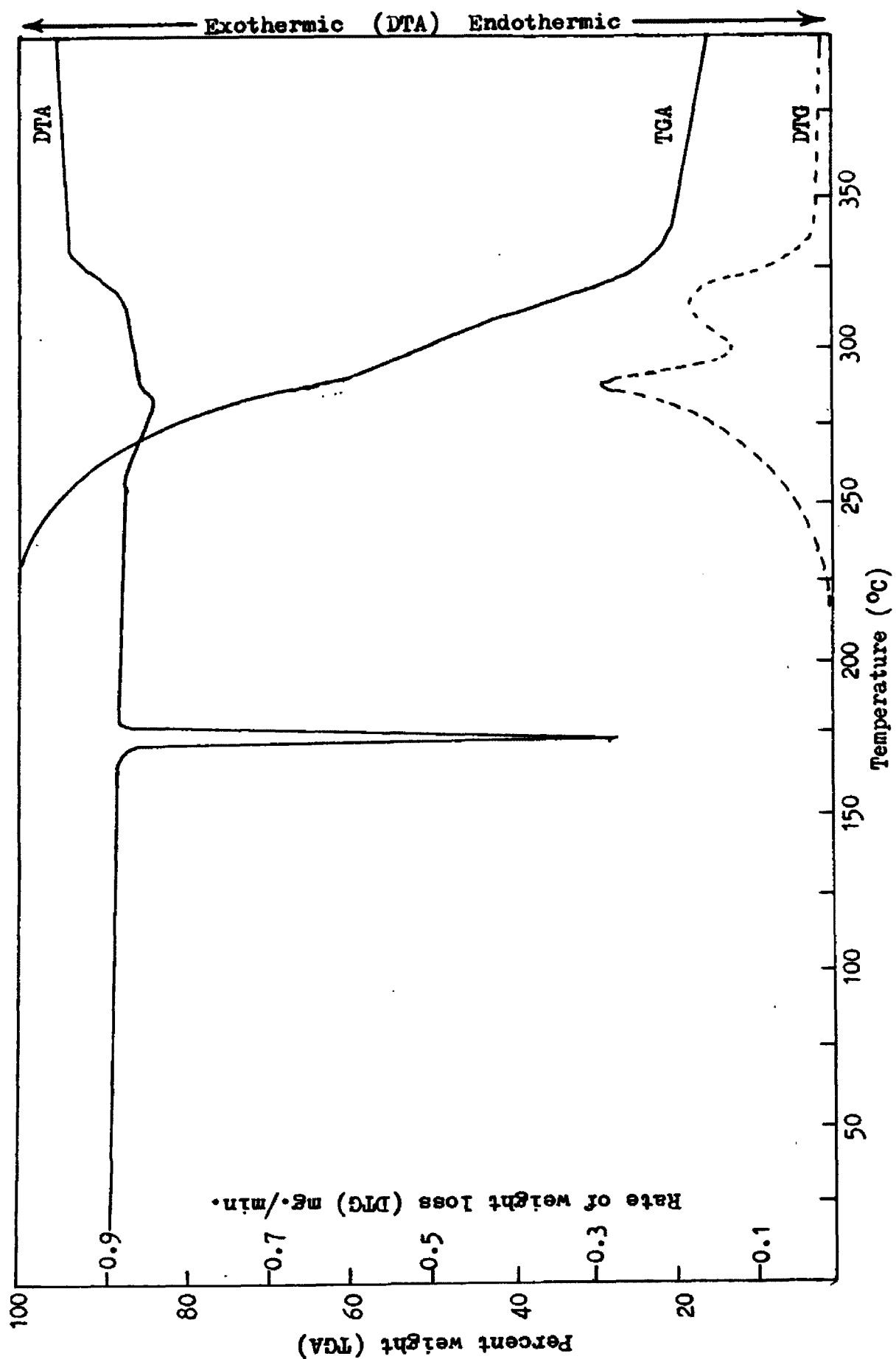


Figure 13.—Thermogram of phenyl β-D-glucopyranoside.

phenyl β -D-glucopyranoside, cleavage of the glycosidic linkage was quantitative; whereas, in the case of phenyl 6-chloro-6-deoxy- β -D-glucopyranoside, only 78% of the theoretical amount of phenol could be detected.

Qualitative Analysis of the Volatile Pyrolysis Products
From 6-chloro-6-deoxy- α -D-glucopyranose and
the Related Methyl and Phenyl Glycosides

Samples of the crystalline 6-chloro-6-deoxy- α -D-glucopyranose, methyl 6-chloro-6-deoxy- α -D-glucopyranoside, methyl 6-chloro-6-deoxy- β -D-glucopyranoside, and phenyl 6-chloro-6-deoxy- β -D-glucopyranoside were heated separately under conditions identical with the dynamic dta and tga. The nitrogen purge gas was bubbled through several different solutions in order to detect the presence of volatile pyrolysis products having certain functional groups.

In order to determine if chlorine was remaining with the carbonaceous residue or being eliminated from the substrate, the volatile pyrolysis products were bubbled through a solution of alcoholic silver nitrate. All four chlorine-containing carbohydrate derivatives used in this study produced a white precipitate (silver chloride) indicating that chlorine was present in the volatile pyrolysis products. In all cases, the temperature at which the white precipitate of silver chloride began to appear corresponded to the temperature of the initial decomposition.

Samples of the halogenated compounds were also pyrolyzed and the volatiles in the nitrogen purge gas were bubbled through a solution of 2,4-dinitrophenyl hydrazine (DNPH). As each compound passed through its decomposition endotherm, the clear orange solution became cloudy and a

precipitate formed. This indicated that a carbonyl compound (aldehyde or ketone) was present in the pyrolysis products. The precipitate that formed was collected by filtration, dried and further analyzed by tlc. The tlc results showed the presence of 5-(hydroxymethyl)-2-furaldehyde, 2-furylhydroxymethylketone, 5-methyl-2-furaldehyde, 2-furaldehyde, and 2-furylmethylketone as components of the volatile pyrolysis products.

The change in the pH of a water trap through which the nitrogen purge gas was bubbled was also measured following the pyrolysis of each of the four compounds to 259°C. The results, measured by wide range pH paper, indicated a sharp increase in acidity from neutral pH to pH=2. This decrease in pH indicated that acids, either mineral acids (HCl) or carboxylic acids were among the pyrolysis products.

Mass spectroscopy of the volatile decomposition products showed the evolution of water, carbon dioxide, hydrogen chloride, methanol and methyl chloride from the methyl glycosides, and phenol from the phenyl glycoside. Maximum rate of liberation of the aglycone (methanol or phenol) was shown to occur at the regions of the thermograms signaling the initiation of the decomposition endotherms; whereas, the reactions liberating water and carbon dioxide continued to accelerate with continued heating. In the cases of the methyl glycosides, methyl chloride appeared simultaneously with the liberation of methanol; thus, indicating that both the chlorine and the aglycone were being eliminated at the onset of decomposition.

Quantitative Analysis of the Volatile Pyrolysis Products
From 6-chloro-6-deoxy- α -D-glucopyranose and the
Related Methyl and Phenyl Glycosides

The nature of the thermal reactions of 6-chloro-6-deoxy- α -D-glucopyranose, methyl 6-chloro-6-deoxy- α -D-glucopyranoside, methyl 6-chloro-6-deoxy- β -D-glucopyranoside, and phenyl 6-chloro-6-deoxy- β -D-glucopyranoside were investigated by the analysis of the decomposition products obtained under isothermal conditions at 300°C and 600°C. The glc of the volatile pyrolysis products from the four chlorinated carbohydrate derivatives are shown in Figures 14-17. The distribution of the major volatile products are listed in Table IV. The volatile pyrolysis products of these samples obtained from isothermal heating at 300°C were analyzed by direct gas chromatography and are listed in Table V. The distribution of the volatile pyrolysis products indicate that extensive dehydration reactions resulting in the formation of furan derivatives are occurring rather than fragmentation reactions.

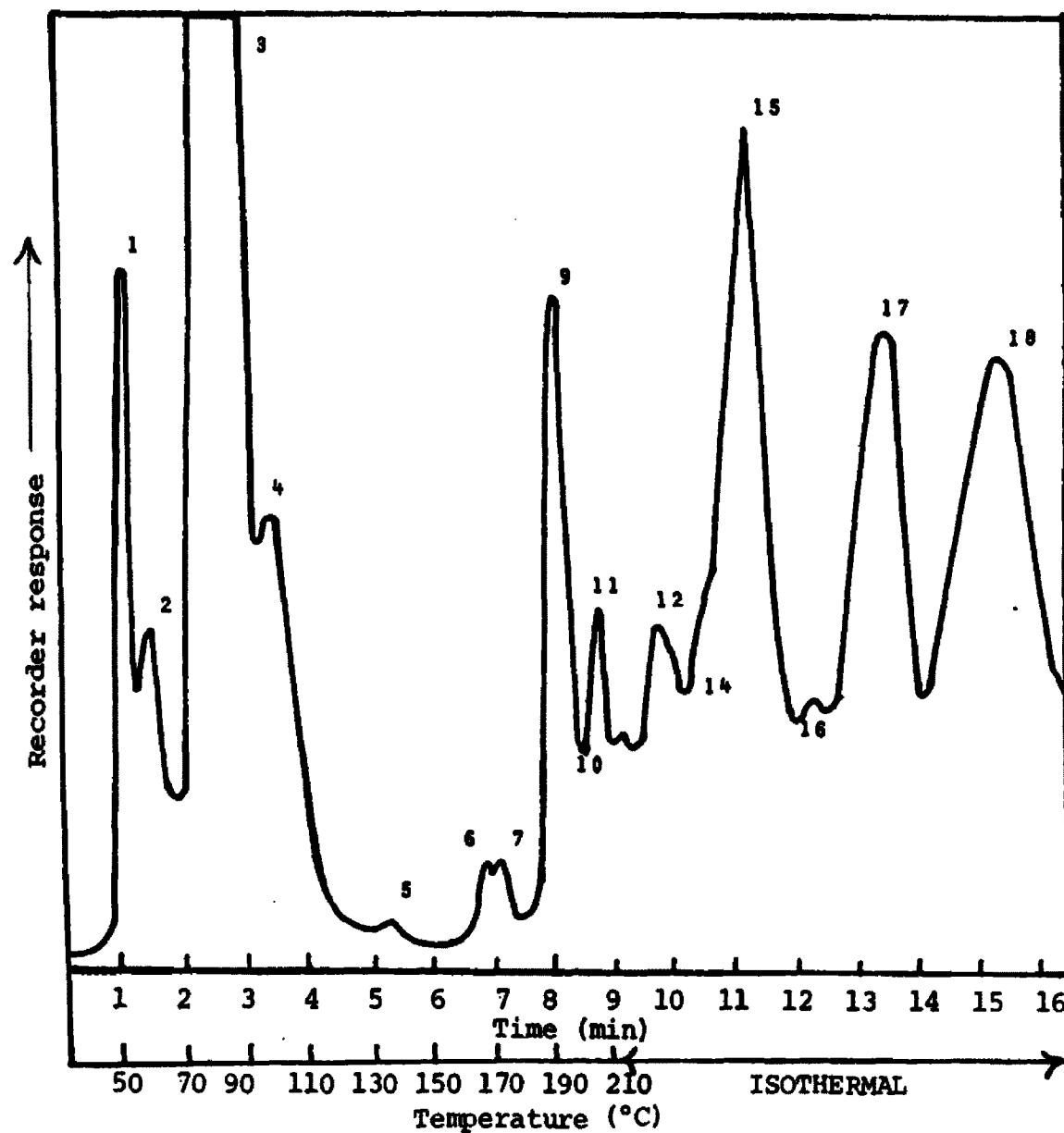


Figure 14.--Chromatogram of products from pyrolysis of methyl 6-chloro-6-deoxy- α -D-glucopyranoside. Composition of the products are listed in Table 5.

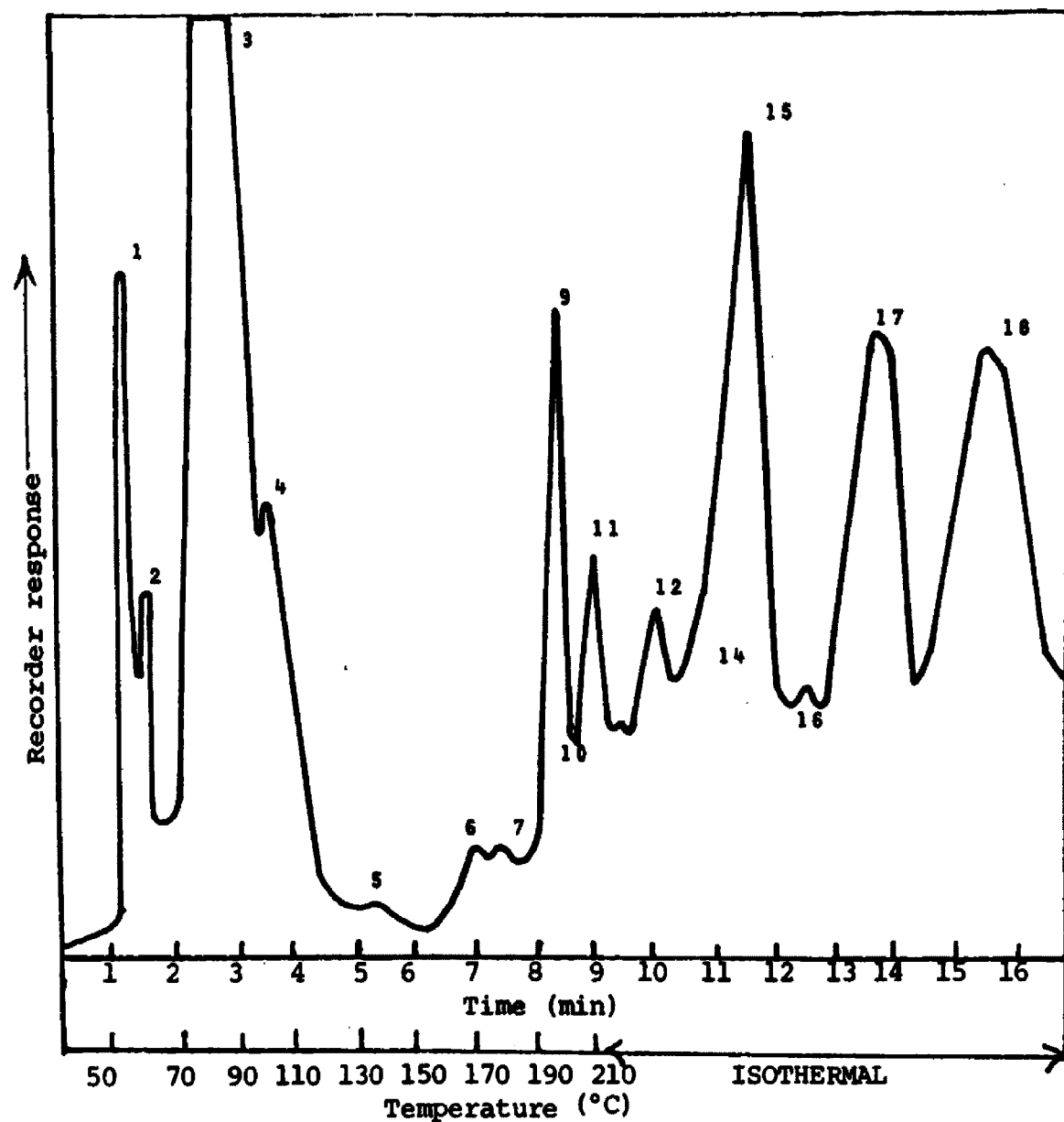


Figure 15.--Chromatogram of the products from pyrolysis of methyl 6-chloro-6-deoxy- β -D-glucopyranoside. Composition of the products are listed in Table 5.

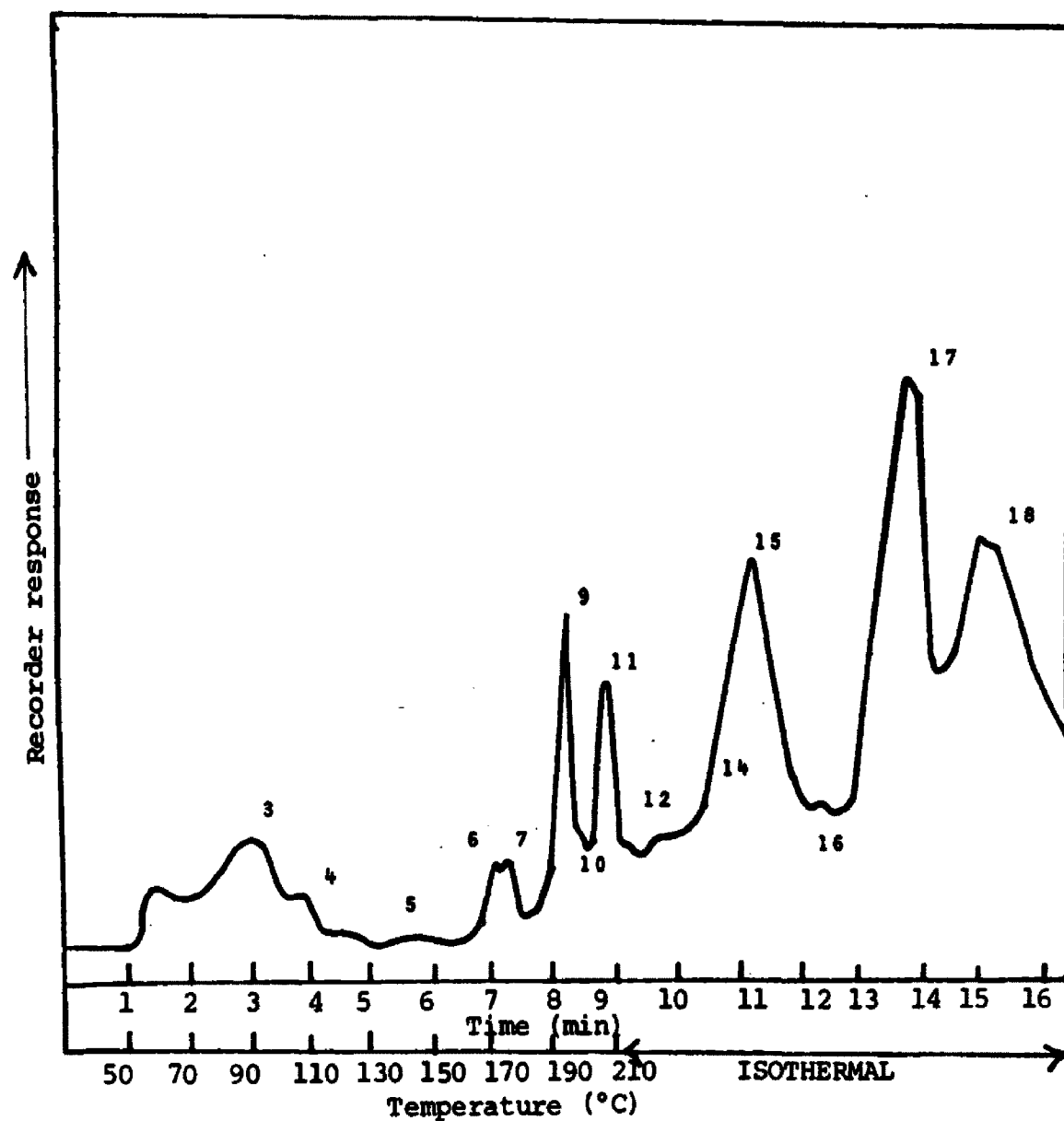


Figure 16.--Chromatogram of the products from pyrolysis of 6-chloro-6-deoxy- α -D-glucopyranose. Composition of the products are listed in Table 5.

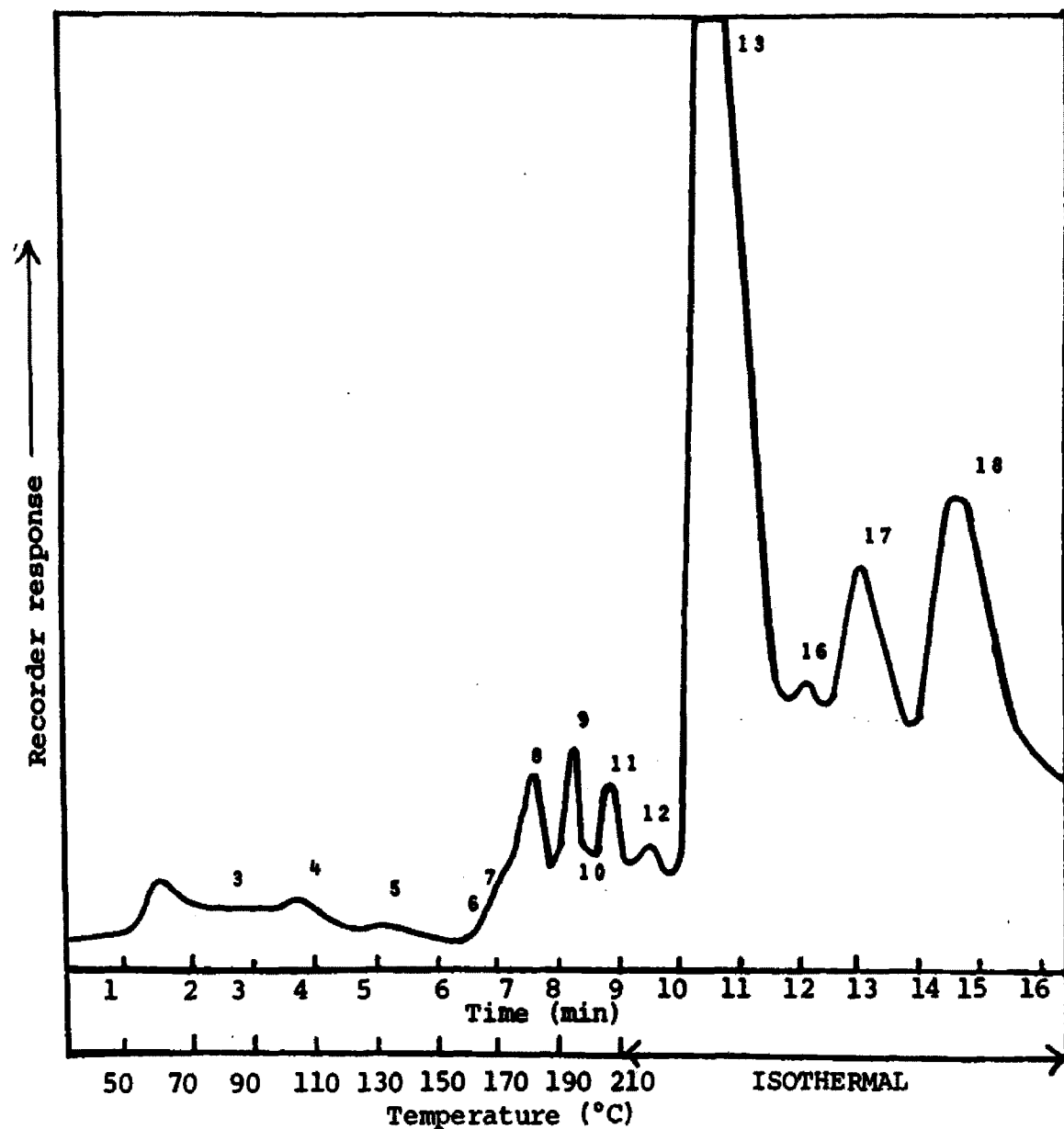


Figure 17.--Chromatogram of the products from pyrolysis of phenyl 6-chloro-6-deoxy- β -D-glucopyranoside. Composition of the products are listed in Table 5.

TABLE IV
PYROLYSIS PRODUCTS OF THE CHLORINATED CARBOHYDRATES AT 400°C

Product ^a	6-chloro- 6-deoxy- α -D- glucopyranose	Methyl 6-chloro- 6-deoxy- α -D- glucopyranoside	Methyl 6-chloro- 6-deoxy- β -D- glucopyranoside	Phenyl 6-chloro- 6-deoxy- β -D- glucopyranoside
Uncondensed gases	9024	14549	20956	6619
Volatile products	4.7	6.4	5.3	3.8
Methanol	T ^b	16.2	17.8	T
Phenol	—	—	—	28.0
H ₂ O ^c	12.0	9.0	9.0	5.0
Char ^d	35	29	32	34
Tar ^e	48.3	39.4	35.9	29.2
TOTAL ^f	100.0	100.0	100.0	100.0

^aUncondensed gases are expressed in units of "number of counts/mg of sample"; the rest are expressed in percentage of "mg product/mg of sample."

^bT refers to trace amounts.

^cWater determined isothermally at 600°C.

^dChar expressed as % residue remaining at 400°C.

^eTar determined by difference.

^fTheoretical yield is 100%.

TABLE V
VOLATILE PYROLYSIS PRODUCTS OF THE CHLORINATED CARBOHYDRATES AT 300°C

Peak No. ^a	Pyrolysis Product	Method of Identification ^b	6-chloro-6-deoxy- α -D-glucopyranose	Methyl 6-chloro-6-deoxy- α -D-glucopyranoside	Methyl 6-chloro-6-deoxy- β -D-glucopyranoside	Phenyl 6-chloro-6-deoxy- β -D-glucopyranoside
—Yield % ^c —						
3	Methanol	1,2	T ^d	16.2	17.8	T
6	Acetic acid	1,2	0.7	1.5	0.9	0.4
7	2-furaldehyde	1,2,3	0.2	0.2	0.2	0.1
8	2,3-benzofuran	1,2	—	—	—	0.3
9	5-methyl-2-furaldehyde	1,2,3	0.7	1.7	1.2	0.6
10	2-furfuryl alcohol	1,2	T	T	T	T
11	α -angelicalactone	1,2	0.6	0.8	0.7	0.4
13	Phenol	1,2,4	—	—	—	28.0
17	Levulinic acid	1	2.5	2.2	2.3	2.0

^aNumber refers to peaks in Figures 14-17.

^bThe numbers refer to identification methods: 1) glc retention time; 2) mass spectrum; 3) tlc of DNPH-derivatives; 4) uv analysis.

^cYield refers to % product based on sample weight.

^dT indicates trace amount.

CHAPTER III

DISCUSSION

The melting endotherms of 6-chloro-6-deoxy- α -D-glucopyranose (Figure 1) and β -D-glucopyranose (Figure 2) are rather wide and unsymmetrical in contrast to the expected sharp melting endotherm of a pure organic compound (Figure 3). A wide and unsymmetrical melting endotherm usually indicates the presence of some impurity or the occurrence of another simultaneous transformation. β -D-glucopyranose is known to anomerize²⁶ during melting as does α -D-xylopyranose¹⁴; thus, this thermal anomerization, or equilibrium of α -D- and β -D-anomeric forms, results in broadening of the melting endotherm.

The results in Table I indicate that as 6-chloro-6-deoxy- α -D-glucopyranose melts, it also undergoes thermal anomerization. The crystalline material is 99.2% pure initially. As the material melts, rapid equilibrium occurs until melting is completed and the ratio of anomers becomes constant. The data from Table I and Figure 1, along with the tlc results, indicate, that, in addition to the molecular rearrangement and equilibration that occurs during melting, 6-chloro-6-deoxy- α -D-glucopyranose also undergoes condensation to form acid hydrolyzable oligosaccharides. Most of the condensation reactions were found to occur in the region of the second endotherm which follows directly after melting. Before the condensation reactions are completed, decomposition begins and continues

with further heating until evaporation of the decomposition products leave a residue of 35% at 400°C. This decomposition is indicated by the rapid weight loss on tga.

The 6-chloro-6-deoxy-D-glucopyranose and related glycosides (Figures 1,3,4,12) are thermally less stable than the parent compounds (Figures 2,5,6,13). This difference in thermal stability indicates that the chlorine atom as a part of the substrate molecule must play a significant role in the thermolysis of these compounds. Considering that normal glycosides initially begin decomposition by cleavage of the glycosidic linkage^{14,15,16} through a transglycosylation process, the large decrease in the threshold decomposition temperatures for the related 6-chloro-6-deoxy compounds indicate that the decomposition reaction is associated with the chlorine atom. Since the mass spectroscopy data of the gases and the alcoholic silver nitrate results indicate that the chlorine atom is being eliminated at the start of decomposition along with the aglycone, the halogen apparently eliminates by a mechanism that results in simultaneous cleavage of the glycosidic linkage. This simultaneous elimination of the halogen and the aglycone points toward a concerted decomposition mechanism rather than a step-wise decomposition yielding a stable intermediate or primary decomposition product.

Considering that 100% (theoretical) free phenol is generated during pyrolysis of phenyl β -D-glucopyranoside compared to only 78% (Table V) from phenyl 6-chloro-6-deoxy- β -D-glucopyranoside, indicates that the normal pyrolytic transglycosylation process is probably being interfered with to some extent. The formation of benzofuran (Table V) from the latter compound indicates that one effect of replacement of the

C-6 hydroxyl with a halogen is to promote cleavage of the carbohydrate ring oxygen in a way similar to the effect from zinc chloride^{14,27} and diphenyl phosphate.²¹ In the case of diphenyl phosphate, it was found that the acidic effect of the additive rather than phosphorylation²¹ was probably responsible for ring oxygen cleavage. This points to the possibility of the halogen being eliminated to form hydrochloric acid which could subsequently catalyze further decomposition of the substrate.

Additional evidence for the formation of an acid catalyst decomposition product is shown by the data in Table III and Figures 7-10. The isothermal heating of methyl 6-chloro-6-deoxy- β -D-glucopyranoside resulted in considerable formation of the corresponding α -anomer. Since a glycoside cannot mutarotate, anomerization of a glycoside is strictly an acid-catalyzed reaction.²⁸ Furthermore, the α -anomer does not begin to appear until after the β -anomer has started to decompose. The existence of such an induction period which increases as the temperature is decreased (Table III) indicates that the decomposition products participate in or accelerate the reaction.¹ In this case, the induction period before formation of the α -anomer probably resulted from the fact that the acidity had not reached a level necessary to catalyze the reaction.²⁹

Although the pyrolysis of cellulose^{30,31} and carbohydrates^{10,11,12,13} is known to produce acids, neither the pyrolysis products, nor zinc chloride^{14,27} tend to produce more than trace quantities of the substrate glycoside's anomeric form. However, the formation of the strong mineral acid, hydrochloric acid, could lead to ring opening and anomerization by an acyclic pathway.^{28,32,33,34}

The thermal stability of normal glycosides has been found to be related to the rate of acid hydrolysis.³⁵ Methyl β -D-glucopyranoside is acid hydrolyzed more rapidly than the α -anomer^{28,32}, and the thermal analysis (Table II and Figures 5 and 6) indicates that methyl β -D-glucopyranoside decomposes slightly faster than the α -anomer. The more rapid rate of acid hydrolysis of the β -anomer has been attributed³⁶ to the higher free energy of the ground state resulting from the anomeric effect, the polar interaction between the equatorial-methoxyl group (β -configuration) and the lone pairs of electrons on the ring oxygen.

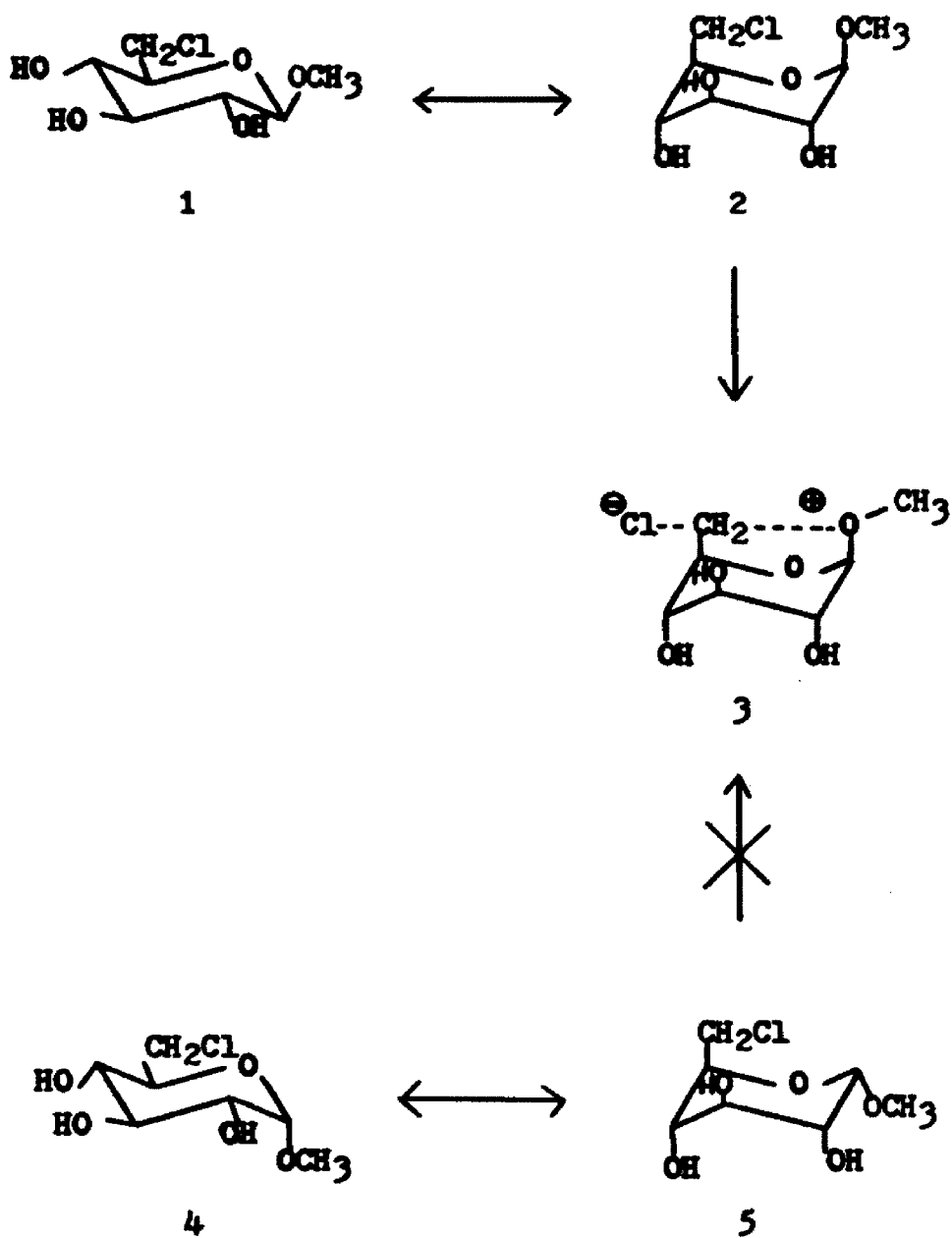
The α - and β -anomers of methyl 6-chloro-6-deoxy-D-glucopyranosides, however, exhibit a much greater difference in thermal decomposition rates (Table II) than observed for the unsubstituted glycosides. The rate of weight loss for methyl 6-chloro-6-deoxy- α -D-glucopyranoside is five times greater than that for the β -anomer. A rapid weight loss during decomposition is indicative of fragmentation reactions; consequently, methyl 6-chloro-6-deoxy- α -D-glucopyranoside is probably decomposing instantly at its decomposition temperature by the thermal elimination or cleavage of certain pieces of the molecule. However, methyl 6-chloro-6-deoxy- β -D-glucopyranoside begins to decompose at a temperature almost 50° lower than that for the α -anomer. Therefore, in terms of kinetics at any given temperature methyl 6-chloro-6-deoxy- β -D-glucopyranoside actually decomposes much faster than the α -anomer. In comparison to the difference in decomposition rates of the normal glycoside anomers, the halogenated glycoside anomers exhibit a tremendous decomposition rate difference.

This pronounced difference in the thermal behavior of the α - and β -anomers of methyl 6-chloro-6-deoxy-D-glucopyranoside (Figures 3 and 4)

and the tremendous difference in decomposition behavior during isothermal heating (Table III) points toward a possible stereochemical difference, a difference in the arrangement of the atoms in three-dimensional space, as being the cause of the difference in reactivity. Since the α -anomer is thermally stable at 160°C but reacts at 220°C while the β -anomer reacts rapidly at 160°C, the tremendous difference in reaction rates indicates that a neighboring-group participation may be involved in the enhanced decomposition rate of the β -anomer.

Normally, neighboring-group participation reactions are observed in solution reactions where the solvent plays a significant role in transferring the ionic charges and promoting intramolecular interactions. Under the thermal conditions employed here, however, the solvent role of the melted sugar is unknown; thus, a neighboring-group participation in the thermal decomposition is particularly interesting. Previously it has been shown that the thermolysis of phenyl β -D-glucopyranoside under alkaline conditions is facilitated by anchimeric assistance of the trans-hydroxyl at the C-2 carbon atom.²³ Consequently, the conformational and configurational effects observed for aqueous systems have been shown to prevail in certain circumstances under pyrolytic conditions.

The only stereochemical difference between the two anomers is the configurational difference that gives rise to the anomeric forms. As shown in Scheme I, for the β -anomer (1), in the 1C chair conformation (2) the aglycone and the C-6 carbon are both cis-axial; whereas, in the α -anomer (4), the 1C chair conformation (5) has the aglycone and the C-6 carbon as trans axial-equatorial. In the former case elimination of the halogen from the C-6 carbon could be facilitated by anchimeric assistance



Scheme I. The anomeric configurations of methyl 6-chloro-6-deoxy- β -D-glucopyranoside (1) and methyl 6-chloro-6-deoxy- α -D-glucopyranoside (4).

of the glycosidic oxygen (3). In the latter case (5), the glycosidic oxygen could not assist in the elimination of the C-6 halogen.

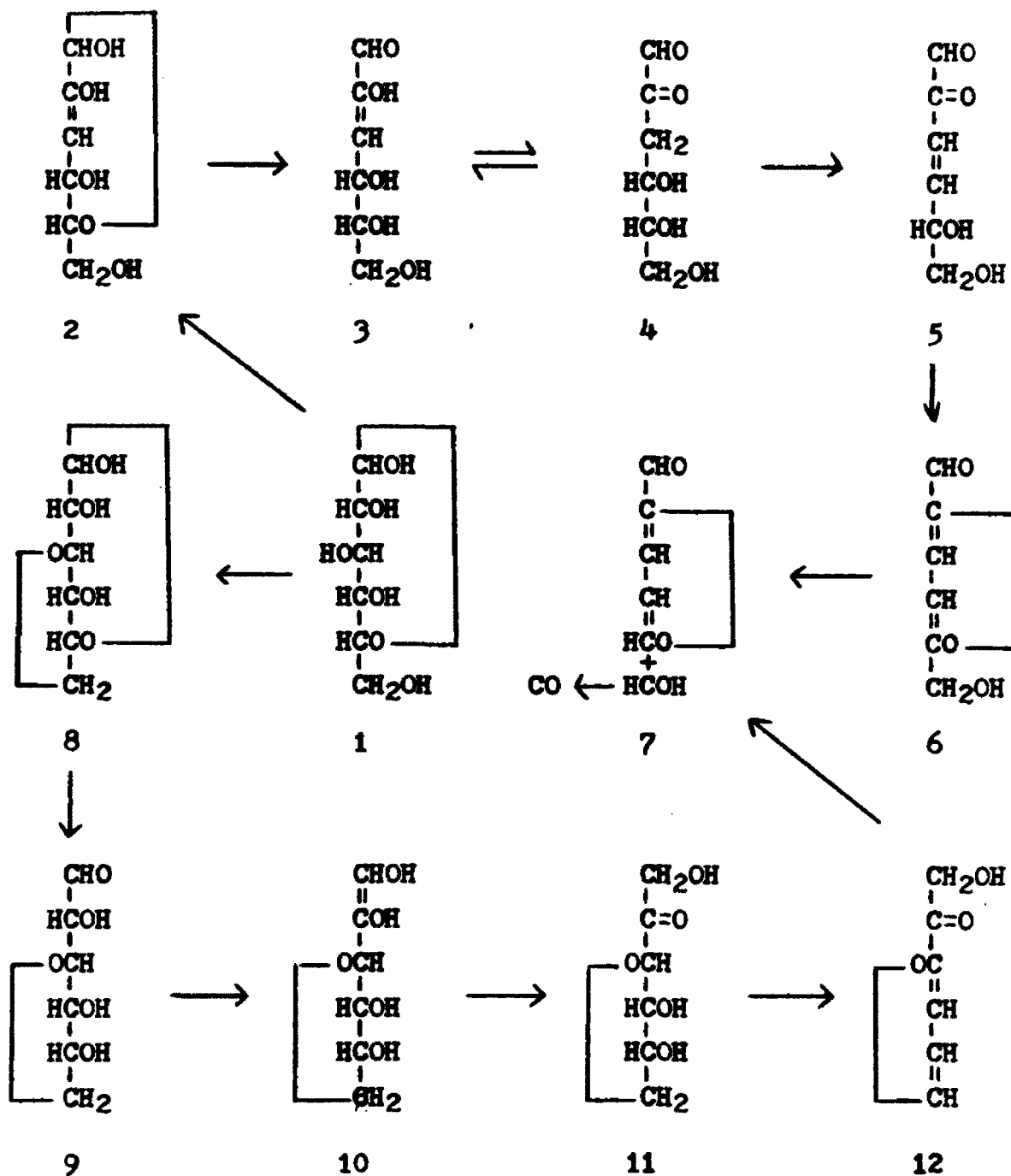
In the case of the β -anomer, the transition state (3) probably consists of a five-membered, cyclic, methyloxonium ion. Anchimeric assistance of the leaving group by the formation of the bridged, methyloxonium ion has been found to be particularly favorable when the intermediate is five-membered.^{37,38} The formation of \underline{D} -glucosyloxonium ions have been reported to be involved in the displacement of certain carbohydrate sulphonates³⁹ and halogens.⁴⁰

The fact that no 1,6-anhydro- β - \underline{D} -glucopyranose was detected even for the thermolysis of 6-chloro-6-deoxy- α - \underline{D} -glucopyranose, which forms the β -anomer on melting, indicates that elimination of the halogen as part of a concerted decomposition reaction is occurring rather than simple nucleophilic displacement of the halogen as would be the case in anhydro sugar formation.⁴¹ If a concerted mechanism were operative, then elimination of the halogen with simultaneous beta-elimination of a hydrogen to form a double bond would be a possibility. A 5,6-unsaturation confers increased lability to the glycosidic group⁴² and simultaneous elimination of the aglycone at this elevated temperature might also be expected. Thus, since the β -anomer could facilitate the elimination of the halogen the reaction may occur at lower temperatures than is the case of the α -anomer where thermal elimination of the halogen is believed to be occurring. Such a mechanism would be consistent with the volatile product analysis which indicated that, in both cases, elimination of the halogen and the aglycone occur simultaneously at the decomposition point.

The volatile products from the thermolysis of the halogenated carbohydrates (Table V) are primarily acid-catalyzed dehydration products of carbohydrates and include furan derivatives, levulinic acid and α -angelicalactone. Since these products result from dehydration of the substrate^{43,44} and not recombination of the carbohydrate fragmentation products, there are two competing pathways, shown in Scheme II,¹¹ for the formation of furan derivatives from the pyrolysis of cellulose, anhydro-sugars and other carbohydrates.^{10,11,12,18,45}

The formation of 5-(hydroxymethyl)-2-furaldehyde (6) involves a 3-deoxy hexosulose intermediate (4) while 2-furylhydroxymethylketone (12) is formed from a 3,6-anhydro intermediate (8). Both of these furan compounds can further break down to yield 2-furaldehyde (7), and it is believed that 5-methyl-2-furaldehyde and 2-furfuryl alcohol are formed from 5-(hydroxymethyl)-2-furaldehyde¹¹ (6). The experimental results (Table V), however, indicate that 5-methyl-2-furaldehyde is formed in a ratio of 8:1 over 2-furaldehyde. Since 5-methyl-2-furaldehyde cannot come from a 3,6-anhydro intermediate, this strongly points toward the fact that the formation of a 3,6-anhydro intermediate cannot be a significant pyrolytic decomposition pathway for the thermolysis of the halogenated compounds.

The formation of 5-(hydroxymethyl)-2-furaldehyde apparently is of fundamental importance in the thermolysis of the halogenated compounds studied since the volatile pyrolysis products (5-methyl-2-furaldehyde, 2-furaldehyde, 2-furfuryl alcohol, levulinic acid, and α -angelicalactone) are in all probability formed from this compound. Additionally, since the halogenated compounds have a halogen replacing the C-6 hydroxyl group, the formation of 5-(hydroxymethyl)-2-furaldehyde would account for the



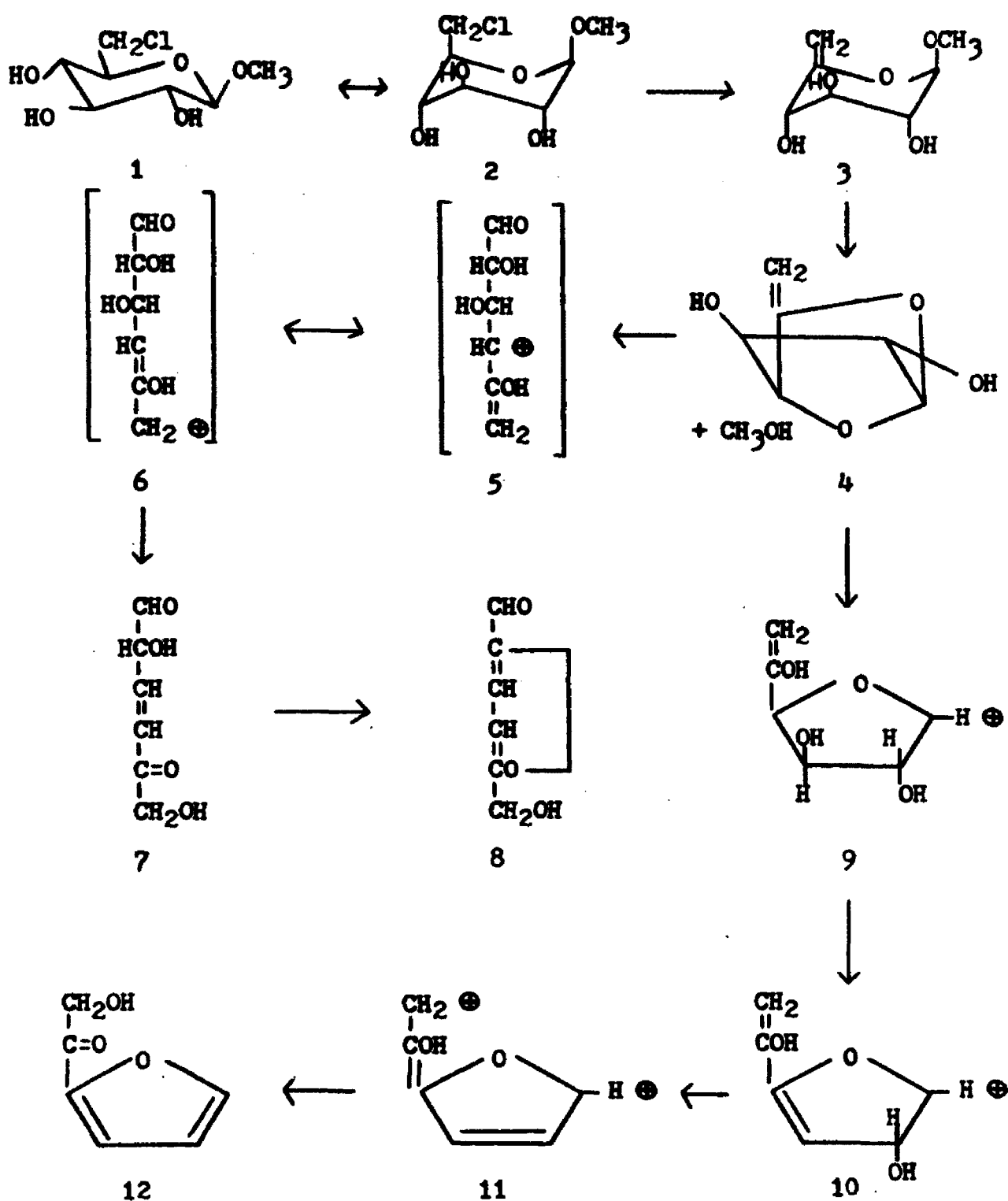
Scheme II.¹¹ The pyrolytic reactions of β -D-glucopyranose.

fact that only slightly more than one molecule of water per substrate molecule is formed during isothermal pyrolysis of the halogenated compounds (Table IV).

The formation of 2-furylhydroxymethylketone need not involve a 3,6-anhydro intermediate since it is possible that this compound could be formed from a 1,4-anhydro intermediate. The formation of 1,4-anhydro intermediates have been postulated for the thermolysis of cellulose and other carbohydrates^{1,18,46,47,48,49,50}, and when the C-6 hydroxyl group was blocked as in the case of tri-O-methyl cellulose, 1,4-anhydro-2,3,6-tri-O-methyl- α -D-glucopyranose was isolated from the pyrolyzate.⁵¹

The thermolysis of the 6-chloro-6-deoxy-D-glucopyranose and related glycosides probably is initiated by simultaneous dehydrohalogenation and elimination of the aglycone. Other than the dehydrohalogenation, this pyrolysis process is similar to that for carbohydrates in general. Elimination of the aglycone would follow an ionic mechanism involving heterolytic cleavage of the aglycone. It seems reasonable, therefore, that this would be a concerted process since charge dispersal in the transition state cannot be stabilized by solvent molecules.

Thermolysis thus consists of inter- and intramolecular transglycosylation reactions. The normal carbohydrate thermolysis transglycosylation reactions are interfered with, however, and a different subsequent decomposition mechanism ensues. In the absence of a C-6 hydroxyl, it would be expected that the C-4 hydroxyl would participate in the concerted ionic elimination of the aglycone to produce a 1,4-anhydro sugar. This process is described in Scheme III.



Scheme III.--The pyrolytic reactions of methyl 6-chloro-6-deoxy- β -D-glucopyranoside.

In the 1,4-anhydro intermediate (4) shown in Scheme III, the C-4 carbon is the allylic carbon with respect to the double bond. Elimination at the C-4 position would be expected to occur with extreme ease due to the allylic stabilization of an intermediate C-4 carbonium ion (5 and 6). The facile formation of 5-(hydroxymethyl)-2-furaldehyde (8) from the intermediate (7) presumably involves the concept of consecutive electron displacement^{52,53} where the driving force is de-enolization (ketonization) of the enolic hydrogen of the C-5 hydroxyl group. Here, ionization of this enolic hydrogen is accompanied by a flow of electrons to the adjacent carbon. Electrical neutrality is maintained by elimination of a group (OH^\ominus) carrying the excess electrons. A benzilic acid type rearrangement (a shift of a group with its binding electrons from one carbon to another carbon) of the hydroxyl from C-3 to C-6 would provide a hydroxyl group for the terminal carbon.

The resulting compound (7) is an α,β -unsaturated ketone which has the correct stereoelectronic requirements for formation of the heterocyclic ring of the furan derivatives. Alternatively, the 1,4-anhydro intermediate (4) could rearrange by a similar series of electron displacement reactions to form 2-furylhydroxymethylketone (12).

The isothermal pyrolysis at 160°C of methyl 6-chloro-6-deoxy- β -D-glucopyranoside followed by uv spectroscopy (Figure 11) indicated that after 1.5 minutes a distinct band with an absorption maximum between 225-230 nm was evident. Continued heating (2.0 minutes) resulted in a very pronounced band at 225 nm, as opposed to little or no change in the band starting to form at 290 nm. Further heating (2.5 minutes), however,

resulted in the band at 290 nm becoming extremely large, along with a continued increase in the absorbance of the band at 225 nm. Both bands increased with further heating.

Furan derivatives have a chromophoric group that absorbs in the region of 285-290 nm. Since this band forms after the band at 225 nm it is probable that the compound producing the intense absorbance at 228 nm is an intermediate from the decomposition reaction. An α,β -unsaturated ketone^{54,55,56} has a base absorbance in the uv of 215 nm with 12 nm being added for each beta-substituent. Since the intermediate (7) in Scheme III is an α,β -unsaturated carbonyl with one beta-substituent, the expected absorbance for intermediate (7) would be 227 nm. Thus, the spectroscopic evidence tends to indicate that the thermolysis of methyl 6-chloro-6-deoxy- β -D-glucopyranoside results in the formation of α,β -unsaturated carbonyl compounds which is consistent with the mechanism proposed in Scheme III.

The melting point of crystalline methyl β -D-glucopyranoside (Figure 6) is preceded by an endothermic (dta) transition at 106°C. The transition is accompanied by a 0.5% weight loss (tga). Crystalline methyl β -D-glucopyranoside has been found to contain one-half molecule of water of crystallization⁵⁷ and melts at 104-105°C.⁵⁷ According to latter reports, however, the melting point was 108-110°C⁵⁸, and currently the melting point is reported as 115-116°C.⁵⁹

The thermal analysis data for methyl β -D-glucopyranoside indicates that the hydrated material melts with a broad endotherm at 110°C²¹ and is preceded by a transition at 95°C due to the loss of water. Recrystallization of the hydrated material from absolute ethanol at 0°C

followed by drying at 40°C in vacuo for 48 hrs produced the thermogram shown in Figure 6. Insufficient data are available to determine if the transition observed at 106°C is due to the presence of another crystalline form of methyl β -D-glucopyranoside, a possibility which cannot be excluded since carbohydrates are known to exhibit polymorphism and other crystalline transitions.⁶⁰

The melting of methyl α -D-glucopyranoside (Figure 5) is also preceded by a transition (dta) at 155°C that is accompanied by a 2% weight loss (tga). Crystalline methyl α -D-glucopyranoside melts at 165-166°C⁶¹ which is consistent with the melting point of 167°C obtained from the thermal analysis data in Figure 5. In Figure 5, the first endothermic transition at 155°C is followed by a small exothermic peak at 162°C. This succession of endothermic and exothermic peaks is a characteristic feature⁶⁰ of a transformation involving melting of a metastable form of the crystalline material and subsequent crystallization of the stable form. Although x-ray diffraction data was not obtained which could confirm the existence of different stable and metastable forms, thermal analysis data from another sample of methyl α -D-glucopyranoside⁶² did not exhibit this transition at 155°C. It is possible that different recrystallization conditions could account for the formation of stable and metastable forms of methyl α -D-glucopyranoside.⁶⁰

CHAPTER IV

EXPERIMENTAL

Analytical methods. Melting points were determined with a Fischer-Johns apparatus and are uncorrected. Thin layer chromatography (tlc) was performed on silica gel 1B-F (Bakerflex) irrigated with (A) methanol-benzene (1:5), (B) ethyl ether-benzene (1:5), (C) benzene-tetrahydrofuran (98:2). The spots were detected by spraying with 10% sulfuric acid in methanol followed by heating at 120°C for 10 minutes or by spraying with ethanolamine. Gas-liquid chromatography (glc) was performed with a Varian 1800 instrument equipped with hydrogen flame detectors. The column used to separate the methyl 6-chloro-6-deoxy-D-glycosides after heating and trimethylsilylation was a 6 ft X 0.125 in stainless steel tubing packed with Varaport 30 as the support and 3% OV-17 as the stationary phase. After trimethylsilylation, the 6-chloro-6-deoxy-D-glucopyranose compounds were separated on a similar column using 3% SE-30 as the stationary phase. The volatile pyrolysis products were analyzed using a 12 ft X 0.125 in stainless steel tubing packed with Fluoropak 80 as the support and 10% 20M carbowax as the stationary phase. Quantitative data were obtained by using a Varian Model 475-470 digital integrator calibrated with standard samples. Water was determined on a modified Perkin-Elmer Pyrolysis Unit²¹ attached to an F and M Model 5750 glc having thermal conductivity detectors. The column was a 12 ft X 0.25 in stainless steel tubing packed with Fluoropak 80 as the support

and 10% 20M carbowax as the stationary phase. UV analysis was performed on a Hitachi EPS-3T ultra violet spectrophotometer. Mass spectroscopy was performed on a Varian-Mat III spectrometer at 80 ev.

Sample preparation. The 6-chloro-6-deoxy-D-glycosides were prepared by a modification of a previously described method.⁶³ The parent glycoside (19.4 g) was dissolved in DMF (200 ml) and cooled to 10°C in an ice bath. Methane sulfonyl chloride (37.5 ml) was added dropwise, then the solution was heated on an oil bath at 70°C \pm 5° for 16 hrs. n-Propanol (37.5 ml) was added and solution was kept at 70°C for 3 hrs. The solution was concentrated under reduced pressure at 60°C first with a water aspirator, then with an oil pump. The cooled solution was diluted with 500 ml H₂O, stirred at room temperature for 1 hr, then concentrated at 60°C to a sirup. The sirup was dissolved in acetic anhydride (125 ml), warmed to bring into solution and stirred overnight. The reaction mixture was poured onto cracked ice (500 ml) and stirred to induce crystallization. The product was collected by suction filtration, decolorized with carbon, recrystallized from 95% ethanol and dried in vacuo at 30°C for 48 hrs:

Methyl 2,3,4-tri-O-acetyl-6-chloro-6-deoxy- α -D-glucopyranoside, recrystallized from abs ethanol; mp 98-99°C (lit.⁶⁴ mp 98-99°C); R_f (solvent A) 0.75; R_f (solvent B) 0.38.

Methyl 2,3,4-tri-O-acetyl-6-chloro-6-deoxy- β -D-glucopyranoside, recrystallized from abs ethanol; mp 138-139°C (lit.⁶⁵ mp 141°C); R_f (solvent A) 0.73; R_f (solvent B) 0.34.

Phenyl 2,3,4-tri-O-acetyl-6-chloro-6-deoxy- β -D-glucopyranoside, recrystallized from abs ethanol; mp 145-146°C; R_f (solvent A) 0.81; R_f (solvent B) 0.46.

The compounds were catalytically deacetylated using 0.03 M NaOCH_3 in absolute methanol, followed by neutralization with DOWEX-50W-X8 H^+ ionic form resin beads. The methanolic solutions were concentrated to dryness using a water aspirator, recrystallized at 0°C from a suitable solvent and dried in vacuo at 30°C for 48 hrs:

Methyl 6-chloro-6-deoxy- α -D-glucopyranoside, recrystallized from ethyl acetate; mp 113-114°C (lit.⁶⁴ mp 110-112°C); (lit.⁶⁶ mp 113-114°C); R_f (solvent A) 0.27.

Methyl 6-chloro-6-deoxy- β -D-glucopyranoside, recrystallized from abs ethanol; mp 156-157°C (lit.⁶⁵ mp 156-157°C); R_f (solvent A) 0.24.

Phenyl 6-chloro-6-deoxy- β -D-glucopyranoside, recrystallized from H_2O ; mp 169-170°C; R_f (solvent A) 0.44.

1,2,3,4-tetra-O-acetyl-6-chloro-6-deoxy- α -D-glucopyranose was prepared as described previously.⁶³ Methyl 6-chloro-6-deoxy- α -D-glucopyranoside (5.87 g) was dissolved in a solution of acetic acid (180 ml), acetic anhydride (24 ml) and conc. sulfuric acid (9 ml), and kept for 70 hrs at room temperature. The reaction mixture was poured onto crushed ice (500 ml) and stirred to induce crystallization. The crystals were

collected by suction filtration, washed with H_2O , dried, recrystallized from ethyl ether at $0^\circ C$, and dried in vacuo at room temperature for 48 hrs:

1,2,3,4-tetra-O-acetyl-6-chloro-6-deoxy- α -D-glucopyranose, recrystallized from ethyl ether; mp $163.5-164^\circ C$ (lit.⁶³ mp $164^\circ C$); R_f (solvent A) 0.71; R_f (solvent B) 0.33.

Deacetylation was accomplished by dissolving 1,2,3,4-tetra-O-acetyl-6-chloro-6-deoxy- α -D-glucopyranose (3.59 g) in absolute methanol (100 ml) at $0^\circ C$. 0.1 M sodium methoxide in abs methanol (20 ml) was added and kept at $0^\circ C$ for 16 hrs. The solution was neutralized with DOWEX-50W-X8 H^+ ionic form resin and the methanolic solution was evaporated to a sirup at $40^\circ C$ using a water aspirator. The sirup was dissolved in 1:5:5 (abs ethanol-ethyl acetate-ethyl ether) and allowed to crystallize at $0^\circ C$. After several days, white crystals formed which were collected by suction filtration and dried in vacuo at $30^\circ C$ (yield: 0.85 g):

6-chloro-6-deoxy- α -D-glucopyranose; mp $132-135^\circ C$ (lit.⁶⁷ mp $135-136^\circ C$); R_f (solvent A) 0.11; R_f (solvent B) 0.0.

Thermal analysis. The dta data were obtained with a DuPont Model 990 thermal analyzer equipped with a calorimeter cell. All experiments were performed with approximately 1.5 mg samples in covered 6 mm aluminum pans and an empty pan was used as a reference. The cover had a small hole in it to allow volatile products to escape. The samples were heated at $10^\circ/min$ with a 75 ml/min flow of nitrogen. The tga data were obtained

under the same conditions of atmosphere and temperature as the dta data, with a Cahn R-100 Electro-balance used for weighing the samples and the DuPont thermal analyzer used to program a furnace surrounding the sample tube. The derivative of the tga (signal) (dtg) was taken with a Cahn time derivative computer (Mark II).

Thermal decomposition products. The samples were heated under the same conditions as for the dynamic dta, at a rate of $10^{\circ}/\text{min}$ under nitrogen atmosphere to the temperature of various endotherms as in the thermal analysis experiments. The heated samples were then rapidly removed from the dta cell, the reaction was quenched by rapid cooling, the samples were transferred to dry test tubes containing 1,6-anhydro- β -D-glucopyranose (known weight), and "Trisil" (Pierce Chemical Company Product No. 489997; equal volumes of hexamethyldisilazane and trimethylchlorosilane in pyridine) (0.3 ml) was added and the solution was heated on a steam bath for 15 minutes and analyzed by glc.

Isothermal experiments were performed similarly, with the temperature being increased rapidly to the desired temperature and held within $\pm 0.5^{\circ}\text{C}$. The heated samples were analyzed either by trimethylsilylation and glc analysis or by dissolving in methanol and uv or tlc analysis.

Volatile products were analyzed by heating the sample in a similar manner through its decomposition point. The volatiles were quantitatively trapped by bubbling the nitrogen purge gas through 1) 1.0 N NaOH followed by uv analysis for phenol, 2) alcoholic silver nitrate for halogen determination, 3) water followed by pH determination for acids, 4) ethyl ether followed by glc-mass spectroscopy analysis for

identification of volatiles, and 5) 2,4-dinitrophenyl hydrazine (DNPH) in 2 N HCl. The resulting DNPH precipitate was filtered, washed with 1 N HCl and water then dried. The DNPH derivatives of the carbonyl compounds were analyzed by tlc using solvent C. The carbonyl compounds were identified by comparison with known compounds and color developed after spraying with ethanolamine.⁶⁸ Compounds containing free hydroxyl groups were verified by acetylating the DNPH derivatives followed by tlc analysis.⁶⁸

The volatile products evolved at the start of decomposition were monitored by mass spectroscopy.¹³ Samples in 6 mm aluminum pans were heated under helium at 15°/min. The purge gas passed directly into the mass spectrometer.

Direct analysis of the volatile products from isothermal heating was performed by pyrolyzing samples (1.5 mg) at 300°C in a furnace (Varian-Inductor Model 695) attached to the injection port of the gas chromatograph and in a modified Perkin-Elmer pyrolysis unit connected to a gas chromatograph.²¹ The identification methods of resolved compounds included: 1) comparison of the retention time on glc with known compounds, 2) mass spectroscopy of the peak from collected fractions of the volatiles, 3) identification of DNPH derivatives from collected fractions of the volatiles, and 4) uv spectroscopy of the collected material.

CHAPTER V

CONCLUSIONS AND SUMMARY

The results obtained from this study indicate that 6-chloro-6-deoxy-D-glucopyranose and related glycosides are thermally less stable than the parent carbohydrates. The initiation of the decomposition reactions was associated with elimination of the chlorine atom from the substrate, and the overall decomposition of the substrate was autocatalytic. Decomposition was found to involve mainly dehydration and condensation reactions which produce water, char, and furan derivatives. Furthermore, cleavage of the glycosidic linkage was found to be competing with an alternative pathway in which the ring structure is cleaved and the glycosidic group remains attached to a part of the sugar moiety.

The conformational and configurational characteristics of carbohydrates that result in a variety of reactions ranging from mutarotation of the free sugars to extensive rearrangement and degradation in solution, were also found to prevail when the 6-chloro-6-deoxy-D-glucopyranose and related glycosides were heated in the dry state. The 6-chloro-6-deoxy- α -D-glucopyranose underwent thermal anomerization as it melted, and the β -anomer of the 6-chloro-6-deoxy-D-hexoses eliminated the chlorine atom by anchimeric assistance involving a glycosyloxonium ion. Reactions involving shifts of electron pairs including enolization and de-enolization reactions also occurred during pyrolysis.

The sequence of the decomposition reactions was followed and unraveled by coordinated thermal analysis and parallel chemical investigations involving mass spectroscopy, ultra violet spectroscopy and chromatography. The results provided the basis for a scheme which rationalized the formation of the proposed intermediates and the numerous decomposition products. In light of the evidence indicating possible formation of a glycosyloxonium ion and reactions involving shifts of electron pairs, a concerted process for the overall decomposition of the substrate appears favorable since charge dispersal in the transition states cannot be stabilized by solvent molecules.

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